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## **Co-Gasification of High Sulfur Coal with Coal-bed Methane to Produce Synthesis Gas with Adjustable H<sub>2</sub>/CO Contents for Synthesis of Value-added Chemicals**

*A Report submitted to:*

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## 1. EXECUTIVE SUMMARY

This research project is the conceptive development of a process to produce synthesis gas with a flexible  $H_2/CO$  ratio by the co-gasification of coal and coal-bed methane. The feasible  $H_2/CO$  ratio of synthesis gas for production of chemicals is between 1 and 2. Generally the coal gasification process generates synthesis gas with an  $H_2/CO$  ratio between 0.9 and 1.2, depending on property of the coal feedstock and operational modes. Reforming or partial oxidation of methane can generate synthesis gas with an  $H_2/CO$  ratio between 1 and 3. Co-gasification of coal and methane is expected to generate synthesis gas with varied  $H_2/CO$  ratios. However, matching and cooperation between these two reactions in kinetics and thermodynamics must be achieved for the process and quality control of synthesis gas production. The preliminary feedstock includes two Kentucky bituminous coals and simulated coal-bed methane. For comparison purposes, two other low rank coals of the United States (U.S.) are also used in tests of gasification. They are Lignite and Powder River Basin (PRB) coal, which is a Sub-bituminous coal. Steam, composed of air or oxygen, is used as an gasification agent in coal gasification and co-gasification processes of coal with methane. Catalytic performance of ashes and chars, which originally form several Kentucky coals and Lignite and PRB coal, is also evaluated. Through completion of the proposed project, answers to important questions revolving around co-gasification of coal and coal-bed methane in the following areas will be given:

1. How to control the cold gas efficiency (the sum of  $H_2$  and  $CO$ ), conversion efficiency of coal and CBM and adjustability of  $H_2/CO$  ratio of synthesis gas?
2. What are the main constitutes in coal ash that has a catalytic function on coal and CBM co-gasification? What kind of Kentucky coal ash has higher catalytic activity on the co-gasification process? Does the structure of coal char have impact on activity for methane reforming and partial oxidation?
3. Which is the control factor of mercury capture by solid residues of co-gasification, the active site or residue pore structure? How do you control preferable characterization of solid residues produced on mercury capture?

Other specific objectives of the proposed project also include 1) investigation of the chemistry, fundamental mechanisms, and reaction kinetics of coal under gasification conditions and coal-bed methane under reforming or partial gasification conditions; 2) Investigation of the possible cooperative effects among the reactions of the co-gasification process; 3) Determination of the optimum gas-solid contact model and a sound reactor design; mass and heat balance.

A modified lab-scale fluidized bed gasification demonstration unit with ID of 2.5 inches and an enlarged portion of 4 inches was used to conduct all major experiments on gasification of selected coal samples and also co-gasification of coal and coal-bed methane for the process demonstration. The process chemistry, fundamental mechanisms, and reaction kinetics were investigated in a one inch OD test rig. Test results indicated that:

► For all tested coals, co-gasification of coal and simulated methane could generate synthesis gas with the  $H_2/CO$  ratio at nearly 2.0, by which chemicals production through Fischer-Tropsch (F-T) synthesis could be achieved. Carbon conversion efficiencies of KY bit-2 and methane conversion efficiency could be achieved at above 80%, especially in the oxygen-blown mode. Another KY bit-1 shows lower carbon conversion efficiency due to its lower gasification reactivity. It could be improved by extending its residence time at the elevated temperature in the gasifier, such as the high temperature Circulating Fluidized Bed Gasifier (CFBG). The gasification selectivity of coal and methane conversion (the cold gas efficiency in the sum of  $H_2$  and CO) could be achieved at above 80% in the oxygen-blown mode. Two low rank U.S. coals show better reactivity than Kentucky coals, but lower gas yield and gas quality because of higher moisture and/or ash content in these low rank coals. The development of high temperature (less than ash melting temperature) Circulating Fluidized Bed Gasification process (CFBG) seems imperative for all Kentucky coals in the near future.

► Thermodynamics calculation predicts that the methane conversion could be achieved by almost 100% and selectivity (the sum of  $H_2$  and CO) by almost 100% at a temperature range of 900-1050 °C. However, the  $H_2/CO$  ratio is below 1.5 if all possible reactions on  $CH_4$  reforming and partial oxidation occur. The followed-up kinetics study in the one inch testing rig presents the possibility of  $CH_4$  reforming and partial oxidation with a pretty favorable  $H_2/CO$  ratio, which is greater than 5. The higher  $H_2/CO$  in  $CH_4$  reforming and partial oxidation process means less  $CH_4$  in mass needed to adjust the  $H_2/CO$  ratio in the co-gasification process of coal and coal-bed methane, which is efficient. Ash failed to be a good candidate of catalyst on  $CH_4$  reforming and partial oxidation because of its very low specific surface area available for proceeding of catalyst reactions. However, coal chars present very promising catalytic performance on  $CH_4$  reforming and partial oxidation because of their larger specific surface area. In this study no other constituents in coal fly ash or special surface properties of coal chars were correlated with the enhanced  $CH_4$  conversion efficiency. It seems that the specific surface area is only variable in controlling  $CH_4$  conversion efficiency. Another important conclusion in 1" testing rig educated us on the enhanced

contact mode between coal char and methane. In the followed-up tests in the 2.5” gasification demonstration unit, addition of methane is below in the dense phase but above the area where the oxygen concentration is enriched so that the higher CH<sub>4</sub> conversion efficiency and selectivity could be achieved in this study.

► Mercury and potentially solid residues, which are both generated in the gasification process could be enacted by EPA rules because they are dangerous to our environment. In this study, a conceptive development of Hg capture by char residues from gasification process was pursued. Tests indicated that gasification char residue could be re-activated by steam to generate effective Hg adsorbent with its developed pore structure. Most promisingly, all activated char residues, which were derived from Kentucky coals, generally showed enhanced Hg capture capability and even better than char residues from low rank coal. It was likely that the sulfur species on the surface of activated char residue enhanced Hg capture by strong bonding between sulfur and Hg. Low rank coal is generally used to prepare good adsorbent because of its activation reactivity resulting in the larger specific surface area with less production cost. Char residues, which were derived from gasification process of Kentucky coals, could be good candidates for preparation of Hg adsorbents.

## 2. BACKGROUND

Most coal beds are permeated with methane ( $\text{CH}_4$ ), which is commonly referred to as coal-bed methane (CBM).<sup>1</sup> Methane is a potent greenhouse gas, with 21 times the global warming potential of carbon dioxide.<sup>2</sup> Methane release from coal mining accounts for approximately 10% of methane emissions in the U.S.<sup>3</sup> Recovery of CBM can mitigate a large source of greenhouse gas emissions, while allowing for an economic use of the energy source.

CBM is gaining strong interest nationally, and the Southeast is a particularly promising market because of its large gas demand and the Appalachian basin's many CBM-rich coal seams.<sup>4</sup> Currently, pipeline quality CBM is being sold to distribution systems in the Appalachian coal basin. CBM has the potential to make seven states at least partially self-sufficient with regard to their gas supply.<sup>4</sup> The coal mines of Eastern Kentucky are on the border of the Appalachian coal basin. Thus, CBM supply in Kentucky can be locally competitive with conventionally produced pipeline natural gas. Kentucky Governor Ernie Fletcher stated earlier this year that the General Assembly of Kentucky had passed into law CBM initiatives.<sup>5</sup> **Also, in Kentucky's Comprehensive Energy Strategy Plan,<sup>6</sup> Coal-Bed Methane was categorized as an emerging opportunity with potential deposits of at least 848 billion cubic feet reported by the Kentucky Geological Survey. In this strategy plan, Recommendations 39 through 41 are focused on the survey, production, and utilization of CBM.** It is distinctly pointed out in Recommendation 41 of this strategy plan that "The Commonwealth of Kentucky should identify the potential of coal bed methane value-added industries and, if feasible, design economic development strategies to grow those industries around the State's coal bed methane reserves."

One area that could benefit from CBM is the production of synthesis gas ( $\text{H}_2+\text{CO}$ ), which can be used as a feedstock for production of high value chemicals.<sup>7</sup> Generally, synthesis gas ( $\text{H}_2+\text{CO}$ ) can be produced through coal gasification, and methane and hydrocarbon reforming or partial oxidation.<sup>8</sup> With the decline of oil resources (hydrocarbon mixtures), natural gas including CBM seems to be the most suitable route for synthesis gas production. However, economically viable processes based on natural gas or CBM for manufacturing synthesis gas typically produce a gas that is too rich in hydrogen ( $\text{H}_2/\text{CO}=3$ ) to meet the stoichiometric ratios required by major synthesis gas based chemicals which is 2 for most chemical syntheses.<sup>9</sup> Some other value added chemicals may require the  $\text{H}_2/\text{CO}$  ratio of the synthesis

gas to be varied between one and two.<sup>7</sup> Thus, H<sub>2</sub>/CO adjustment units are necessary prior to downstream chemical synthesis. The synthesis gas manufacturing systems based on natural gas are also capital intensive due to the presence of an expensive catalyst and higher energy consumption. Hence, there is growing interest in the development of an alternative technology for cost-effective synthesis gas production based on methane as the feedstock. Furthermore, synthesis gas production based on coal provides synthesis gas with H<sub>2</sub>/CO at a ratio of one. Co-Gasification of CBM and coal may provide synthesis gas with suitable H<sub>2</sub>/CO for chemical synthesis.

Direct production of synthesis gas with a flexible H<sub>2</sub>/CO ratio, which is in agreement with the stoichiometric ratios required by major value added chemical synthesis, can decrease the capital investment and the operating cost. Co-gasification of coal and methane is a new concept to produce synthesis gas with a flexible H<sub>2</sub>/CO ratio economically by optimizing the process schemes and applying non-catalytic conditions. This concept has been put forward by several authors.<sup>10-11</sup> Cao and Wu co-gasified coal and methane to produce hydrogen-rich synthesis gas (H<sub>2</sub>/CO ratio greater than 1) in a fluidized-bed reactor<sup>10-11</sup>. Cao focused on the behavior of coal's sulfur release under a hydrogen-rich environment during co-gasification. The achievable H<sub>2</sub>/CO ratio was about 1.5-2 under the air blown condition. In fact, direct production of a flexible H<sub>2</sub>/CO synthesis gas may be achieved by optimizing the process schemes during co-gasification of coal and methane based on different routines.

The Institute for Combustion Science and Environmental Technology (ICSET) at Western Kentucky University (WKU) will be establishing a laboratory-scale gasification unit with Eastern Kentucky Power Cooperative/Warren Rural Electric Cooperative's gift (\$250,000). The gasification system will be used to develop a number of important gasification programs, including Advanced Gasification Synthesis Multi-Contaminant Cleanup Technologies and Novel Gasification Concepts, such as Chemical Looping Gasification and Co-Gasification Technologies. Based on the technical insights of previous and current programs, including some positive preliminary results at ICSET and the requirements of Kentucky's Comprehensive Energy Strategy on CBM utilization, a new process is proposed to co-gasify coal with CBM to produce synthesis gas with an adjustable H<sub>2</sub>/CO ratio economically. Additional benefits may include the economical abatement of sulfur emissions and the production of a potential mercury adsorbent. This process is based on some key chemical reaction mechanism and its cooperative effects. This project will also strive to develop advanced technologies to reasonably utilize both coal and CBM sources and



to reduce their environmental impact as indicated in Governor Ernie Fletcher's 2005 Comprehensive Energy Strategy.

The proposed research will provide a portfolio for economic and environmental utilization of Kentucky CBM and high sulfur coal to produce the feedstock of value-added chemicals. The project's research results will help to understand the catalytic nature of Kentucky coal ash for gasification of coal and CBM; sulfur transformation; control of high-sulfur Kentucky coal; and mercury capture mechanisms of co-gasification residues. The demonstrated co-gasification technology will not only help to preserve Kentucky's and the nation's environmental quality, but also will open new markets for Kentucky's coal and CBM.

### 3. TEST METHODS

**3.1 Survey of U.S. and Kentucky Coal Coal-bed Methane (CBM).** Kentucky has been one of the top three coal production States in the United States for the last 50 years. Its yearly coal production reached 119.0 million tons in 2004. This is high-rank bituminous coal with a higher BTU heating value. The leading coal producer is Wyoming with a yearly coal production (mainly Sub-bituminous coal) of 396 million tons. The leading Lignite producer is Texas, which produces 45 million tons of Lignite yearly. Wyoming Sub-bituminous coal has very low sulfur content, but lower BTU heating value due to its higher moisture content. Texas Lignite has a higher content of sulfur, ash and moisture, thus lower BTU and quality. All three typical U.S. coals, which can represent three typical U.S. coals at different ranks, have high volatile content<sup>12</sup>. U.S. coal provides 52% of the electricity in this country and in Kentucky 91% of our electricity comes from coal<sup>12</sup>.

Coal-bed methane (CBM) is regarded to be one of the Nation's most abundant fossil fuel resources. Conservative estimates suggest that in the contiguous United States more than 700 trillion cubic feet (TCF) of coal-bed methane exists in place, with 100 TCF economically recoverable with existing technology – equivalent to about a 5-year supply at present rates of use<sup>13</sup>. Coal-bed methane now accounts for about 7.5 percent of total natural gas production in the U.S. The Powder River Basin area, including Wyoming and Montana, is one of the newest, most productive areas of coal-bed methane activity in the U.S. This area is the top producer of PRB sub-bituminous coal in the U.S. Another major coal-bed methane production area is in the Black Warrior Basin in Alabama, which is close to the geological reserve of Texas lignite<sup>14</sup>.

Although there is currently no CBM production in Kentucky, a reconnaissance study has indicated that coal beds in both Eastern and Western Kentucky could potentially produce economic CBM<sup>15-16</sup>. Currently, there are two on-going projects in Western Kentucky to assess this potential. Collected petrographic data is consistent with previously published data for coals in Union, Webster and Ohio Counties in Kentucky. The deposition data indicates that the gas content is smaller than the gas content of CBM projects in the Pocahontas coal of Kentucky, Virginia and West Virginia. But its CH<sub>4</sub> purity is greater than that of CBM in the Powder River Basin. Gas isotope data indicated that the gas present in the coal is relatively pure (over 90% methane). Based on the survey of the potential geological reserves of

co-production of coal and CBM in the study, we selected three kinds of coals at different ranks, which are Kentucky coals, Wyoming PRB coal and Texas Lignite to conduct co-gasification tests.

**3.2 Preparation and Characterization of Coal, Char and Ash.** This study focuses on Kentucky coals. Considering the possible application of current technologies, the other two U.S. typical low-rank coals, including Lignite and Sub-bituminous coal (Powder River Basin - PRB) were also included during investigations. Thus, a total of five U.S. coals with different ranks were selected and tested for this study at different stages, including three Kentucky Bituminous coals with different sulfur content; one Lignite coal; and one Sub-bituminous PRB coal. The coals, which were originally used for pulverized coal combustion, were supplied by coal-fired utilities. Coal samples were first pulverized in the WKU ICSET's coal preparation area (shown in Figure 1) and sieved into coal fines or particles with an average diameter of 250 $\mu$ m (100-500 $\mu$ m) and 650 $\mu$ m (500-850  $\mu$ m). Coal samples were dried in an oven, whose temperature was maintained at about 100 °C overnight before testing. Their proximate and ultimate analysis of coal samples are shown in Table 1-1. Analysis results of their minor oxides are shown in Table 1-2. Test methods followed ASTM standard methods D5142 for moisture, ash, and volatile matter. D5373 was used for analysis of carbon, hydrogen, and nitrogen content of coal samples. D4239 was used for analysis of sulfur content in coal samples. Other methods include: D4208 for chlorine content; D3761 for fluorine content; D6722 for mercury content; and D5865 for heating value. A Rigaku energy dispersive X-ray fluorescence (XRF) spectrometer was used to analyze the minor oxide contents of fly ashes by following ASTM Method D4326. The loss on ignition (LOI), as well as carbon and sulfur contents in the ash samples, were determined using ASTM Methods D5142, D5373, and D5016, respectively. Mercury content in coal char and ash samples were analyzed using the LECO AMA-254 analyzer by following the ASTM standard Method D6722. The AMA-254 analyzer has a 0.01-ng mercury detection limit; a working range of 0.05-600 ng; a reproducibility of <1.5%; and a 5-minute? analysis time.

As indicated in Table 1-1, all tested coals have high volatile contents. The volatile content of three Kentucky Bituminous coals is about 35 % on a dry basis. Their moisture content is 2.5% on average on a air dry basis, which is much lower than those of low rank coals. All three Kentucky coals have slightly higher ash content than PRB coal, but much lower than that of Lignite. Of all tested coals, Kentucky coals have the highest BTU values. PRB coal has the lowest sulfur coals and KY bit-3 has the highest sulfur content among all tested coals. The other two Kentucky coals have similar sulfur content as that of Lignite. As indicated in

Table 1-2, PRB coal has a relatively high content of CaO and MgO in its ash. Correspondingly, sulfate content is also higher due to higher reactivity of CaO and MgO for sulfur capture. KY bit-3 has much more iron oxide in its ash. The other three coals, including Texas and two Kentucky coals, have similar ash constituents.

A Micromeritics<sup>®</sup> ASAP<sup>TM</sup> Accelerated Surface Area and Porosimetry were applied to characterize the specific surface area of solid samples. A Micromeritics<sup>®</sup> Chemisorb<sup>TM</sup> 2720 Chemisorption Analyzer was applied to characterize the surface active chemical sites of solid samples. A Micromeritics<sup>®</sup> Elzone II 5390 V1.03 is applied to characterize the particle-size distribution of solid samples. A JEOL LSM-5400 Scanning Electron Microscope, was applied to characterize the surface diagrams of solid samples and simultaneously detect element distribution on surface of solid samples.

**3.3 Test Facilities.** In this study, several facilities were used to conduct the proposed test matrix. A 2.5 inch in ID Gasification Demonstration Unit was utilized to evaluate gasification or co-gasification performance of selected coal samples. A 1 inch in OD test rig was set up to evaluate partial oxidation and reforming of coal-bed methane and gasification of coal char. TA Instruments<sup>®</sup> 2950 TGA were used to evaluate gasification reactivity of coal chars. A 1 inch Hg adsorbent Evaluation System was used to evaluate the Hg adsorbents. Measurement instruments include: two gas analyzers (a Shimadzu GC and a an IMR 6000 multi-gas analyzer) for synthesis gas measurements; S; PSA Semi-continuous mercury monitor for mercury measurements for adsorbent evaluation; Scanning Electron Microscope (SEM); X-ray diffractometer (XRD); and a Pyrolysis-Gas Chromatography-Mass Spectrometer(PY-GC-MS).

*2.5 inch ID Co-gasification Demonstration System.* The project was conducted in a 2.5 inch ID lab-scale fluidized bed coal gasifier, which was set up with previous funding from Eastern Kentucky Power Cooperatives (EKPC) and Warren Rural Electric Cooperative. To allow this facility accommodate to the co-gasification process in this study, several major modifications were made. The first modification was the feeding system for the simulated CBM. An adjustable vertical injector nozzle was installed through the bottom ash discharge opening of the gasifier. The adjustability of the CBM feeding system provided the flexibility required to adjust the injection location of the CBM. The CBM injection location had to be separated from other gasification or reforming agents since methane can explode when mixed with air or oxygen. The second modification was the feeding system for the Kentucky Bituminous coals. During tests in this study, it was found that Kentucky coals had a tendency

to agglomerate during pyrolysis and gasification due to a quick release of its high volatile content. A special set up was attached during tests with Kentucky coals, which was used to pursue the pre-oxidation procedures. The pre-oxidation procedure better controlled the release rate of volatile materials during Kentucky coals testing, and thus was capable of maintaining the continuous feeding of Kentucky coals.

The modified fluidized bed coal gasifier system has seven major components, as shown in Figure 1. They are: a coal feeder; several gasification agent feeders; an ash collector; a fluidized bed coal gasifier unit; a synthesis gas cleanup facility; an air pollutant multi-control test unit; and a waste gas burner coupled with a wet scrubber. The temperature, the pressure and the flow rates of gasification agents of the whole facility are monitored and controlled by thermocouples, pressure gauges and mass flow controllers. Air was supplied by a compressed air line. The steam came from a water-injection pump coupled with an oven operated at 300 °C and 15 PSI. Nitrogen stream was used for system start-up and shut-down. Methane in 100% purity was supplied by a methane cylinder tank. Under an oxygen-blown mode, the 100% pure oxygen stream was supplied by an oxygen cylinder. Trace of Nitrogen stream was used in this mode of operation to calculate synthesis gas yield. The gasification agent streams, except CH<sub>4</sub> stream, were preheated and continuously fed into the gasifier unit through the cone-shaped gas distributor. The coal feeding rate was controlled by a volumetric screw feeder. Two Kentucky bituminous coals and two other low rank U.S. coals were tested in this demonstration unit. The fluidized bed gasifier was 48 inch tall with ID in 2.5 inch. There were two outlets for coal char collection. Except for a common outlet for synthesis gas with char fins, there was a special overflow port on the top of the dense phase in this fluidized bed. It was used to maintain residence time of coal char in the bed. The adjustability of residence time of coal char in the bed could be achieved by changing the coal feeding rate. This gasification was designed to achieve approximately 90% carbon conversion efficiency and above 80% cold-gas efficiency. Variations of these two parameters in actual tests are dependent on test conditions and tested coals. Generally the lower cold-gas efficiency was found at the small testing facility due to its larger heat loss. The char residue, within synthesis gas at the top outlet of gasifier was collected by combining the cyclone and a filter. The cleaned and cooled synthesis gas was collected by a sampling bag and was delivered to gas analyzers.

At the beginning of the test, the fluidized bed gasifier was electrically heated to 700 °C in the protection of the N<sub>2</sub> atmosphere. The fluidized bed gasifier was operated at a velocity of

5-10  $U_{mf}$  (minimum fluidization velocity). After finishing the test, nitrogen was again fed into the bed to replace the gasification agents. The char produced was discharged from the bed and collected as the bed temperature was below 100 °C. In the continuous feeding model, the char produced was continuously discharged and collected in the protection of nitrogen gas. For every testing condition, two parallel tests were conducted. Collected coal char samples were analyzed three times to obtain the average analysis results. If no abnormal results were found, the average data was accepted for certain testing conditions.

*One Inch OD Test Rig for Evaluation of Partial Oxidation and Reforming performance of CBM.* A separate quartz tube furnace of 1 inch in OD, as shown in Figure 3, was used for evaluation of catalytic performance of fly ashes and coal chars. The methane reforming experiment system id consist of four parts: electric furnace, 1 inch OD fluidized bed reactor, steam generator, cylinders of CH<sub>4</sub>, CO<sub>2</sub> and air and control unit. The fluidized bed reactor was made of quartz and has a length of 600 mm with a porous quartz plate placed 300 mm from the bottom. The temperature was measured 30 mm above the porous quartz plate. The steam generator was composed of a syringe pump, a syringe, and a heating tube. The heating tube included a stainless steel tube, heating tape, glass bead and septum. The septum had a sealed function for water and gas. The glass bead in the pre-heater can maintain the temperature of the pre-heater and promote the conversion of water into steam. The heating tape was used to heat the whole steam generator system. This steam generator provided the desired flow rate of steam for the experiment. The flow rate of this system ranged from  $\mu\text{m/hr}$  to ml/min. The flow rate of methane, air, carbon dioxide, and nitrogen was controlled by the mass flow controller. Methane with steam or CO<sub>2</sub> or air was fed into a tube furnace as a gasification agent. The H<sub>2</sub>, CO and Methane with varied gasification agents and temperatures were monitored at the outlet of the tube furnace in order to understand kinetics of catalytic reaction occurrence.

In the experimental procedure, we first introduced nitrogen into the reactor for one hour. We then added activated char (or fly ash), supply methane (or carbon dioxide, or air) and steam in sequence into the reactor, and then the temperature of the reactor was at the point of 700 °C, 800 °C, 900 °C, and sometimes to 950 °C by each run?. Gas and solid residue samples were collected at different temperatures. The gas samples were then sent to a GC analyzer.

*One Inch OD Hg Adsorbent Evaluation System.* This reactor was also used to evaluate mercury capture by gasification residues or their activated products, as shown in Figure 4.

PSA Cavkit was used as the mercury resource to generate mercury for the test. A PSA semi-continuous monitor at the outlet and inlet of the tube furnace was used to monitor mercury concentrations. The mercury concentration differences were used to calculate mercury capture efficiency by co-gasification residues. The temperature of the reactor was set at about 150 °C, and the mercury stream was balanced with nitrogen gas.

*TGA.* Samples of approximately 10-50 mg were placed in a ceramic pan in a TA Instruments model 2950 TGA and heated from ambient temperature at 30-300 °C/ min to a range of 1000 °C. The experiments were carried out in ultra-high purity (UHP) CO<sub>2</sub>, H<sub>2</sub>O or UHP N<sub>2</sub>. The actual test conditions were dependent upon the test purpose. Some experiments having a 30-60 min isothermal hold at the end of the heating segment to monitor continued mass loss. A calcium oxalate experiment was used to confirm the correct operation of the TGA prior to running the samples. The following parameters were measured during testing: time (min); heating rate (°C/min); weight loss (%); weight loss rate (%/min); and the corrected heat flow of the reaction (w/g).

*XRD.* A THERMO ARL X'TRA X-ray diffractometer using Cu KR radiation was used to analyze each of the samples. A tube voltage of 40 kV and a tube current of 20 mA were used for each sample. The samples were scanned every 0.04° from 20 to 90°. The XRD patterns were identified using a database of over 80,000 inorganic compounds. Because the amounts of solid residue samples are required by gram level, a small fixed-bed facility was applied to produce solid residue samples, which were subjected to the XRD analysis.

*SEM.* The samples were prepared by being doped onto carbon tape. The SEM analysis was performed using a JEOL LSM-5400 SEM. The instrument operating parameters were as follows: electron beam energy, 15 keV; working distance, 30 mm; and sample tilt angle, 0°. In most cases, two magnifications at 200\_, 500\_, 2000\_, and 10000\_ were selected to be analyzed.

*PY-GC-MS Technique.* This characterization technology integrates two instruments online: a CDS 5200 pyrolyzer and Varian 2200 GC/MS instrument. The Varian 2200 consists of a Varian 3800 GC and Varian 2200 Ion Trap MS. The MS has a scan range of 10-650 amu. The scan rate was dependent upon the scan range. In the pyrolysis system, the pyrolyzer temperature was kept at 900 °C for 30min. During the experiment when the Tenax TA trap was desorbed and the GC trace obtained, the polymer was held at 30~40°C. During the trapping stage, the Tenax TA was held at about 40 °C. In the GC/MS system, helium was the carrier gas and the capillary column used was DB-5: 30m × 0.25mm × 0.25µm. The split



ratio of the injector was 1:20. The temperature of the transfer line was 300 °C. The GC oven conditions used were as follows: initial temperature of 30 °C for 5 min, ramped to 300 °C at 10 °C/min, held at 300 °C for 10min.

*Synthesis Sampling and Measurement.* Dry, clean gas was sampled by a gas sampling bag every 10 min (generally 5 gas samples) after stable condition was reached (the temperatures on the top and the bottom of the gasifier were kept stable under the control of the feedstock and gasification agents). The permanent gas compositions and hydrocarbon constituents (mainly C<sub>2</sub>-C<sub>4</sub>) of synthesis gas were analyzed by a gas chromatograph (model GC-2010, SHIMADZU, Japan) with a TCD detector. A total of three columns were used to separate H<sub>2</sub>, CO, O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> from CO<sub>2</sub> and C<sub>2</sub>-C<sub>4</sub> hydrocarbons through Porapak R column by using argon as the carrier gas. The former stream was further separated through Porapak Q column and the latter through 5A molecular sieve column. Due to the gasification process being controlled under conditions to eliminate tar production, trace amount (always less than 0.2% totally) of hydrocarbon constituents (C<sub>2</sub>-C<sub>4</sub>) were found in fuel gas by GC. Also, no condensation was found in the cooler water during the testing period. Standard gas mixtures of H<sub>2</sub>, CO, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub> were used for 3-point quantitative calibration of GC 2010.



Table 1-1. Proximate and Element Analysis of Coal and Ash Samples, dry basis

	Moisture	Ash	Vol. Mat	Sulfur	Btu	Carbon	Hydrogen	Nitrogen	Oxygen	Chloride	Mercury	Fluoride	Bromide
SampleName	%	%	%	%	Btu/lb	%	%	%	%	ppm	ppm	ppm	ppm
Lignite (0.1-0.5mm)	24.41	22.51	30.21	1.34	6287	36.17	5.76	0.54	33.68	139	0.25	62	N.D.
PRB (0.1-0.5mm)	11.47	4.87	40.99	0.38	10454	62.04	5.43	0.74	26.54	200	0.06	98	N.D.
KY bit-1 (raw)	3.20	11.59	34.47	1.48	12303	70.80	5.18	1.33	9.62	552	0.07	121	N.D.
KY bit-1 (0.1-0.5mm)	2.52	11.52	34.34	1.07	13145	72.82	5.32	1.49	7.78	1046	0.62	33	N.D.
KY bit-1 (0.5-0.85mm)	1.50	11.23	35.34	0.90	12776	69.98	5.24	1.46	11.19	468	0.10	475	N.D.
KY bit-2 (0.1-0.5mm)	2.39	6.37	34.17	0.50	13498	76.94	5.35	1.62	9.22	1180	0.07	97	N.D.
KY bit-2 (0.5-0.85mm)	2.57	7.02	33.46	0.55	13968	76.56	5.33	1.57	8.97	1637	0.07	204	N.D.
KY bit-3 (0.1-0.5mm)	1.48	16.59	36.32	4.79	11716	64.50	4.85	1.06	8.21	196	0.10	451	N.D.
KY bit-3 (0.5-0.85mm)	2.39	16.11	36.11	4.99	11695	65.98	5.02	1.13	6.77	213	0.10	385	N.D.

Table 1-2. Minor metal oxides of coal samples, dry basis

Data is % wt and after Normalization													
	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	K <sub>2</sub> O	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	BaO	SrO	Fe <sub>2</sub> O <sub>3</sub>	MnO	TiO <sub>2</sub>
Lignite (0.1-0.5mm)	< 0.01	1.33	22.28	52.64	7.44	0.85	8.45	0.05	0.11	0.06	5.39	0.04	1.36
PRB (0.1-0.5mm)	0.40	3.79	13.10	23.69	23.20	0.27	27.84	0.82	0.44	0.34	4.89	0.02	1.19
KY bit-1 (0.1-0.5mm)	< 0.01	0.59	31.02	52.67	0.82	1.80	1.03	0.50	0.15	0.20	8.97	0.01	2.24
KY bit-1 (0.5-0.85mm)	< 0.01	0.60	31.75	53.06	0.74	1.77	0.88	0.59	0.14	0.25	8.13	0.01	2.08
KY bit-2 (0.1-0.5mm)	< 0.01	0.54	29.17	58.77	1.07	1.47	1.20	0.09	0.16	0.22	4.28	0.01	3.02
KY bit-2 (0.5-0.85mm)	< 0.01	0.85	31.83	50.44	1.71	2.48	1.86	0.22	0.19	0.28	8.09	0.01	2.04
KY bit-3 (0.1-0.5mm)	< 0.01	0.86	21.52	44.84	4.23	2.23	4.07	0.26	0.06	0.05	20.65	0.03	1.20
KY bit-3 (0.5-0.85mm)	< 0.01	0.88	21.52	44.40	3.50	2.30	2.26	0.25	0.07	0.05	23.54	0.03	1.20

Figure 1. Coal Preparation Area



1-1. Coal sample collection and storage



1-2 Coal crushing and sieving

Figure 2-1. 2.5" Co-gasification Demonstration System

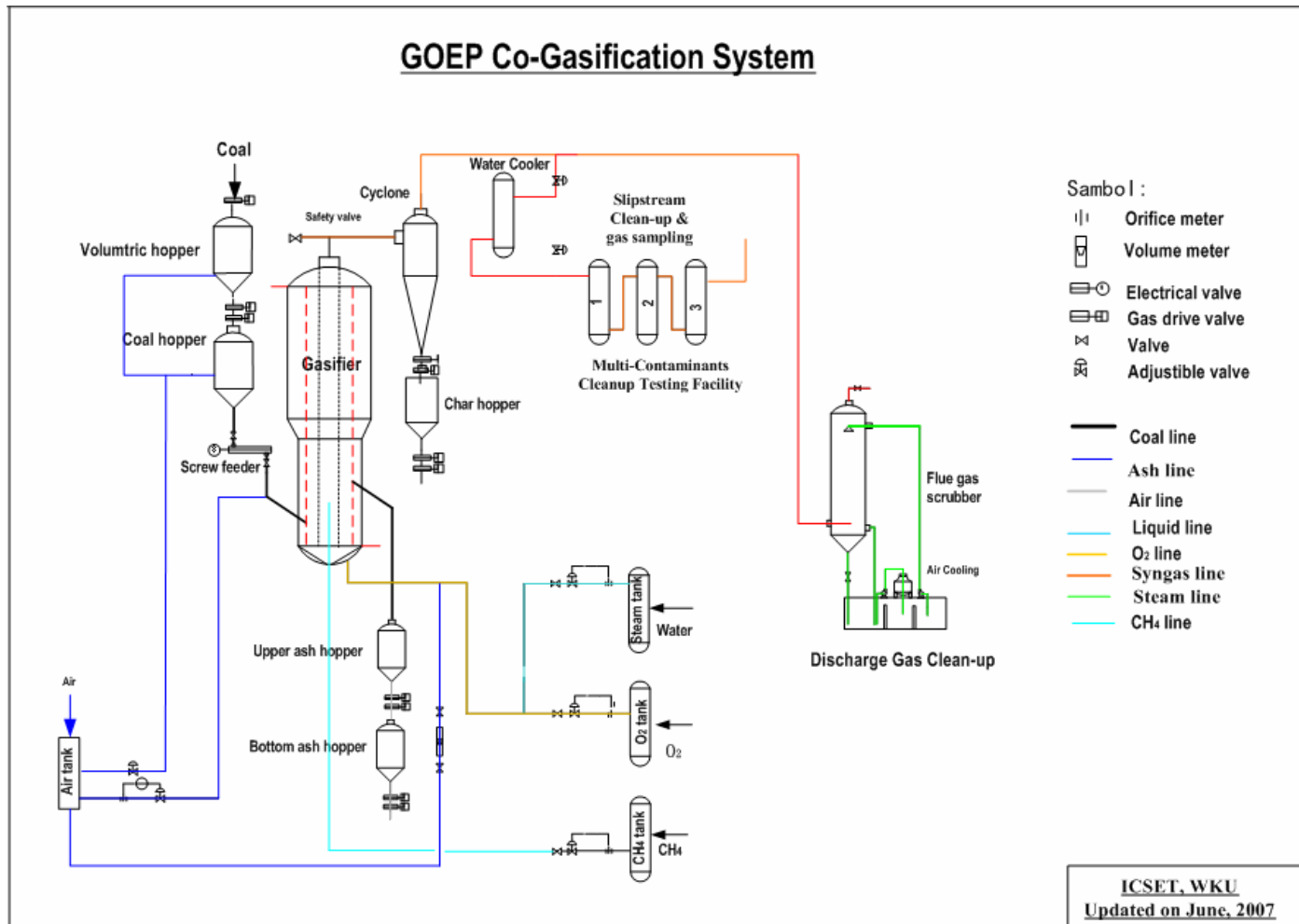


Figure 2-2. Setup Picture of 2.5" Co-gasification Demonstration System



Figure 3. 1" Lab-Scale Evaluation Testing Rigs for Methane Reforming, Gasification

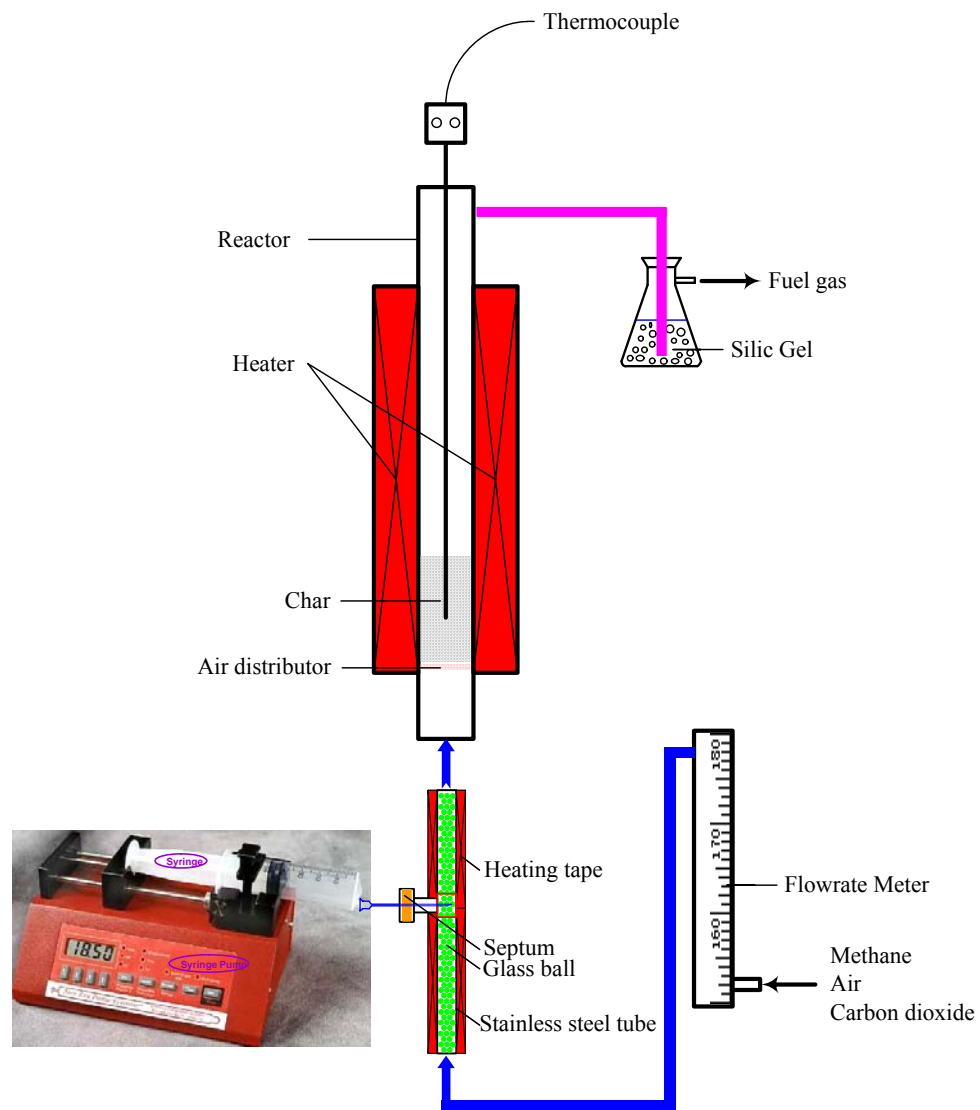


Figure 4. 1" Lab-Scale Evaluation Testing Rigs for Hg adsorbent

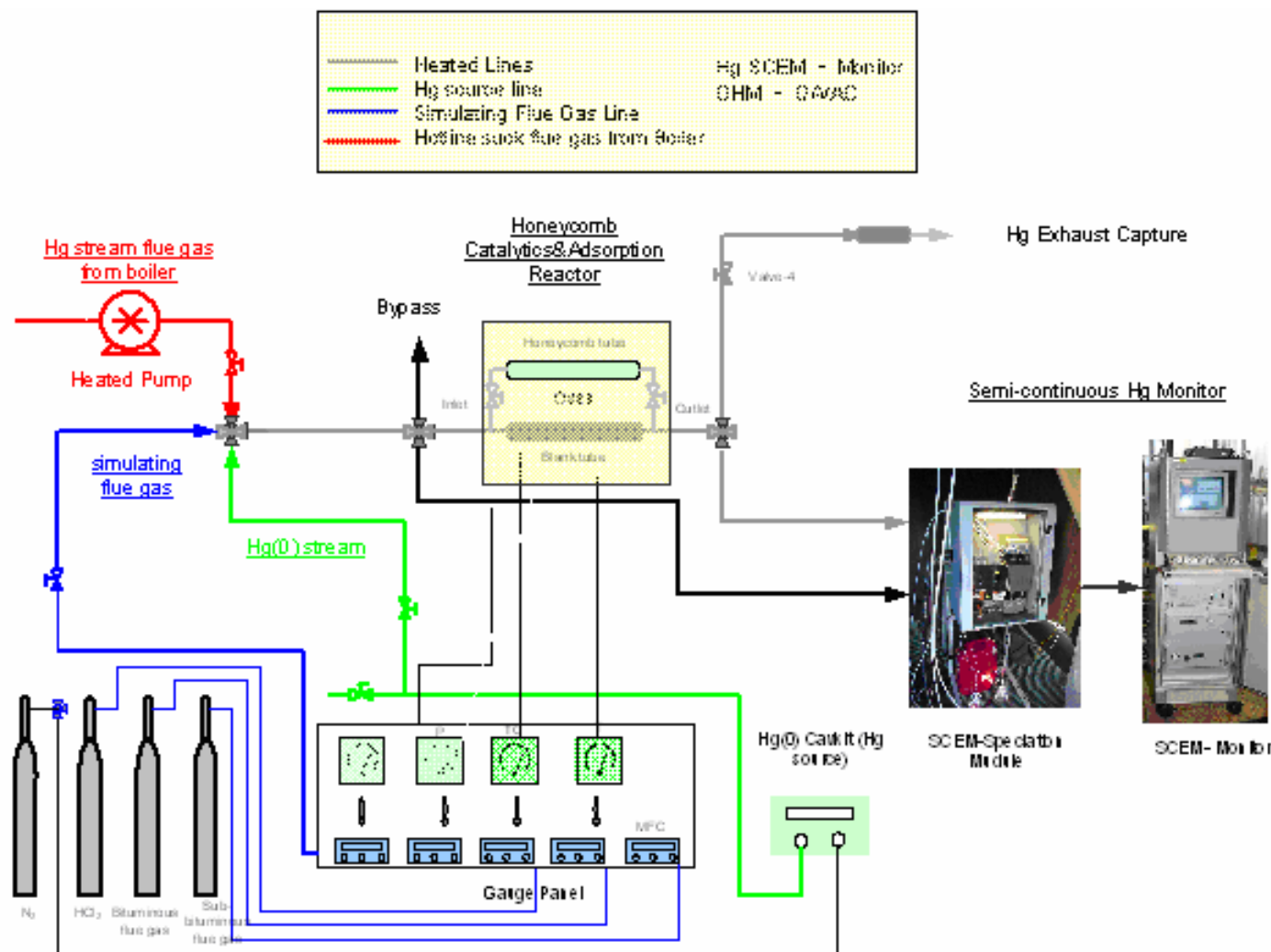




Figure 5. Setup Picture of 1” Lab-Scale Evaluation Testing Rigs for Reforming, Gasification and Hg adsorbent



5-1 Fixed-bed test rig on Char Characterization



5-2. Fluidized-bed Reforming pyrolyzer and gasifier



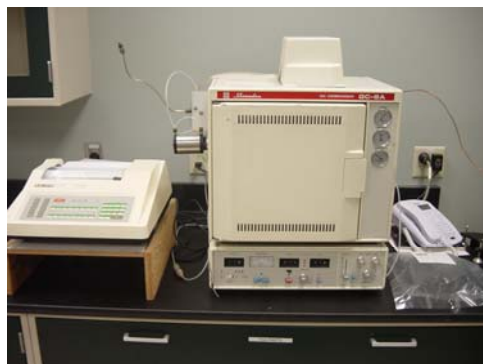
5-3. Hg testing rig on char characterization

Figure 6. Instrumentation for Sample Characterization

6.1 Characterization of Synthesis Gas



1. IMR gasification gas analyzer  
(H<sub>2</sub>S, HCl,.....)



2. GC (H<sub>2</sub>, CO, O<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>)



3. GC-MS

6.2 Characterization of PAH (Liquid)



4. Leeman Unique LC/MS



5. Rotavapor & Nitrogen Evaporator



### 6.3 Characterization of Solid (Char and fly ash)



6. TG or SDT for characterization of char reactivity



7. PY-GC-MS



8. Chemisorp



9. BET surface characterization



10. Leeman ICP-MS for determination of trace metals

## 4. TEST RESULTS

### 4.1 Characterization of Samples of Coals and Coal ashes

The weight loss versus temperature for 5 tested coal samples under  $N_2$  atmosphere is shown in Figure 7-1. The first peaks on the weight loss curves at an elevated temperature corresponded to their moistures loss of tested coal samples. These peaks were larger for Lignite and PRB Sub-bituminous coal and smaller for three Kentucky Bituminous coals that match their moisture content. Second peaks on weight-loss curves correspond to the pyrolysis of coal samples. For two low-rank coals (PRB and Lignite), the onset temperatures of their pyrolysis start early at about 290 °C and their peak temperatures of pyrolysis are at about 470 °C. By comparison, both onset temperatures and peak temperatures during pyrolysis of the three Kentucky coals appeared a little later at about 346 °C and 485 °C on their weight loss curves. Peak heights of three Kentucky coals were almost 2 times larger than those of low-rank coals. It seems pyrolysis of Kentucky Bituminous coals precede at relatively higher temperature and much faster than two low-rank coals. Fast evolvement of pyrolysis materials by Kentucky Bituminous coals resulted in difficulties in continuous feeding of Kentucky coal and in maintaining fluidization during gasification tests.

Figure 7-1. The weight loss verse temperature for 5 tested coal samples under  $N_2$  atmosphere

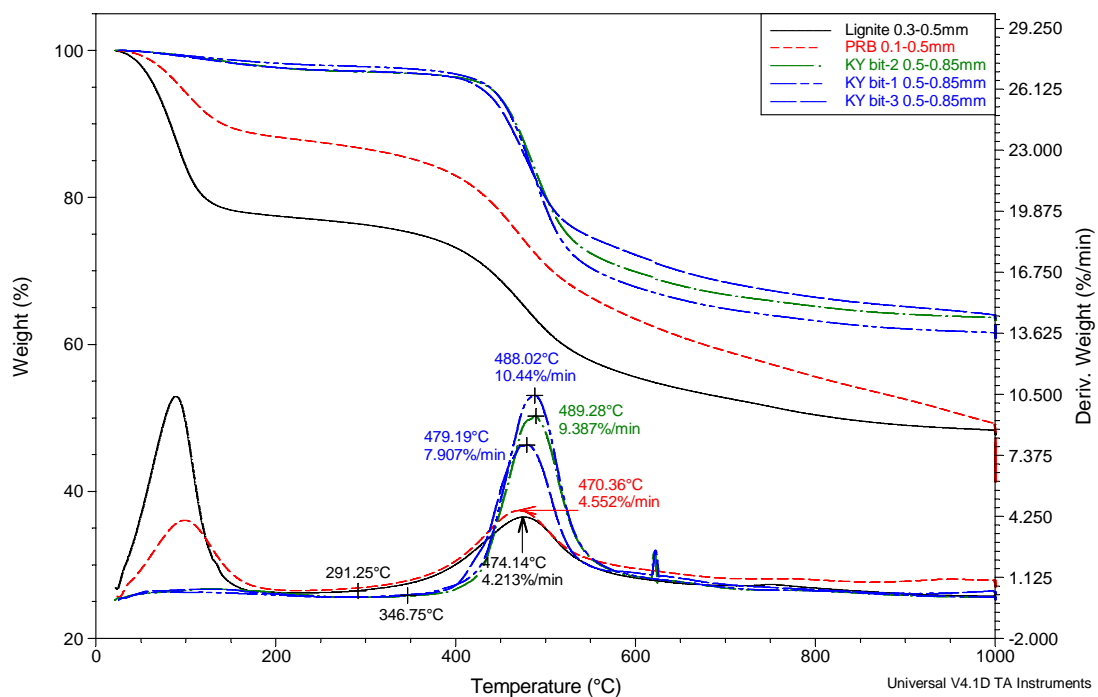
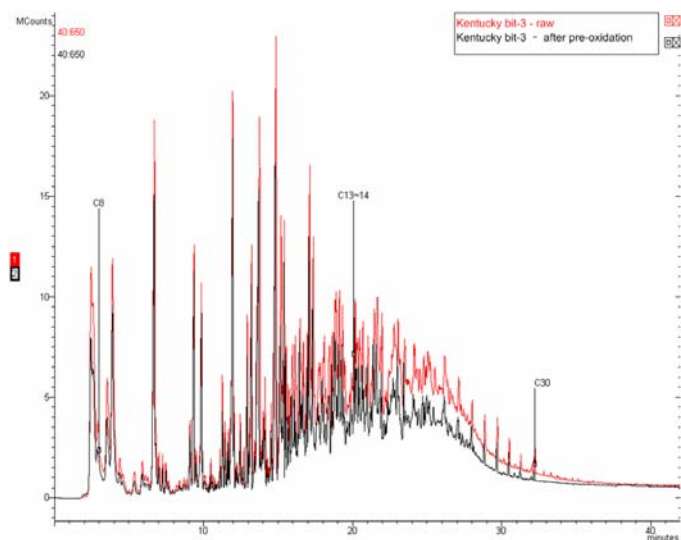
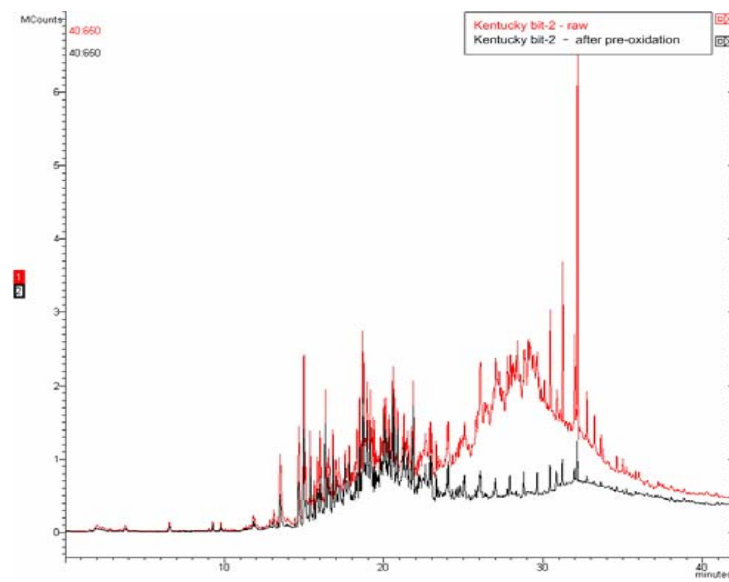
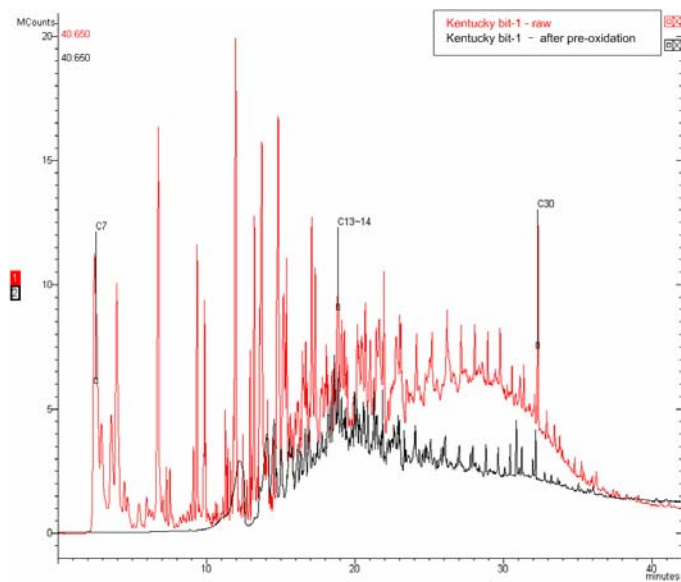


Figure 7-2. Effects of pre-oxidation treatment on pyrolysis products for 3 Kentucky coal samples under N<sub>2</sub> atmosphere



It has been reported that the coal, after oxidation under low temperatures, will result in the reduction of its tar yield and change of its plastic properties during a follow-up pyrolysis process. If so, the pre-oxidation procedures possibly help to work out problems of feeding and fluidization maintenance in the gasifier for Kentucky coals. The answer was positive during tests with three Kentucky coals in the 2.5" demonstration gasifier. The solution to control the quickly evolving pyrolysis products seems to make sense by using the pre-oxidation procedures on Kentucky Bituminous coals. The follow-up mechanical study provided more insight on the impact of pre-oxidation procedures on pyrolysis properties of Kentucky coals. The characterizations of pyrolysis products of Kentucky coals before and after pre-oxidation by PY-GC-MS technology are shown in Figure 7-2. The greater changes on pyrolysis products occurred for KY bit-1 and KY bit-2 before and after pre-oxidation, but less change occurred for KY bit-3. The change after pre-oxidation is shown mainly in the yield of pyrolysis products, of which carbon number is greater than 20. The yield of pyrolysis products, whose carbon number is greater than 20, largely decreased after coal samples were treated by pre-oxidation procedures, especially for KY bit-1 and KY bit-2. There seemed to be no distinct change before and after pre-oxidation procedures for KY bit-3 coal. That means pre-oxidation could not work out the problems of KY bit-3. Finally, we selected KY bit-1 and KY bit-2 Bituminous coals as tested coal samples in the 2.5 inch gasification demonstration unit.

Gasification reactivity of coal chars under atmospheres of two typical gasification agents, such as  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , was evaluated in TGA. Test results are shown in Figure 8-1 and 8-2, respectively. It was found in Figure 8-1 that there were two distinctly different groups in their gasification reactivity (peak heights). Group one includes two low-rank coals (Lignite and PRB) and Group two include three high-rank Kentucky bituminous coals. The gasification reactivity of three high-rank Kentucky coals was much lower than those of two low-rank coals for both gasification atmospheres. The variation of gasification reactivity was also much greater for two low-rank coals as temperature increased than that of three Kentucky coals. Figure 8-2 shows the total conversion efficiency of coal chars under two gasification atmospheres for 30 min. One was 30%  $\text{CO}_2$  and the other was 50%  $\text{H}_2\text{O}$ . Conditions (temperature, residence time and gasification agent concentrations) were set as approximate typical operations by the oxygen-blown mode. It was found that the total conversion efficiency under the  $\text{H}_2\text{O}$  atmosphere was greater than that under the  $\text{CO}_2$  atmosphere. The difference in the total conversion efficiency was greater for three Kentucky coals and smaller for two low-rank coals. It sounds that KY bit-2 coal has greater gasification reactivity than

KY bit-3 coal, and much greater than that of KY bit-1 under both gasification atmospheres. KY bit-2 coal sounds like a suitable coal for the development of gasification or co-gasification processes in this study due to its acceptable reactivity under high temperature.

Figure 9-1. and Figure 9-2. show variation of gasification reactivity under different CO<sub>2</sub> and H<sub>2</sub>O concentrations. It could be found that higher concentrations of gasification agents (either CO<sub>2</sub> and H<sub>2</sub>O) result in higher conversion efficiency and better gasification reactivity of coal char. However, temperatures were the most effective factors in enhancing gasification reactivity for both gasification agents of CO<sub>2</sub> and H<sub>2</sub>O, among other factors such as heating rate and concentrations of gasification agents. Low temperature did not impact gasification reactivity of coal char by varied concentrations of gasification agents. The enhancement of gasification reactivity for PRB started at about 450 °C, which was much lower than three Kentucky coals, which were at about 600 °C under similar CO<sub>2</sub> or H<sub>2</sub>O concentrations. Higher heating rate which was about several hundred °C per min, was always found in the fluidized-bed gasifier. Figure 10. shows the impact of the heating rate of coal char particle on the variation of gasification reactivity. The heating rate increase may have resulted in the decrease of gasification reactivity, especially at a higher temperature range. It was possibly due to annealing of coal char during higher heating rate treatment so that there was a plugging and collapse of pore structure.

Figure 8-1. Gasification Reactivity of Coal Chars under atmosphere of 30% CO<sub>2</sub> or 35% H<sub>2</sub>O

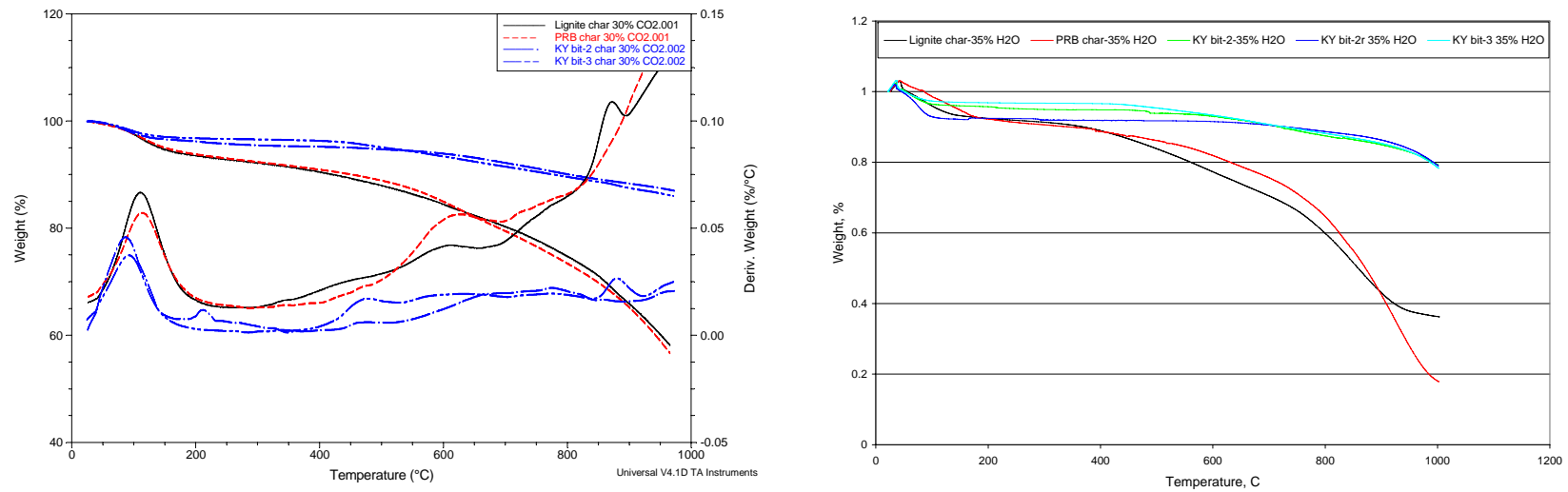


Figure 8-2. Conversion Efficiency of Coal Chars under atmosphere of 30% CO<sub>2</sub> or 50% H<sub>2</sub>O after 30 min

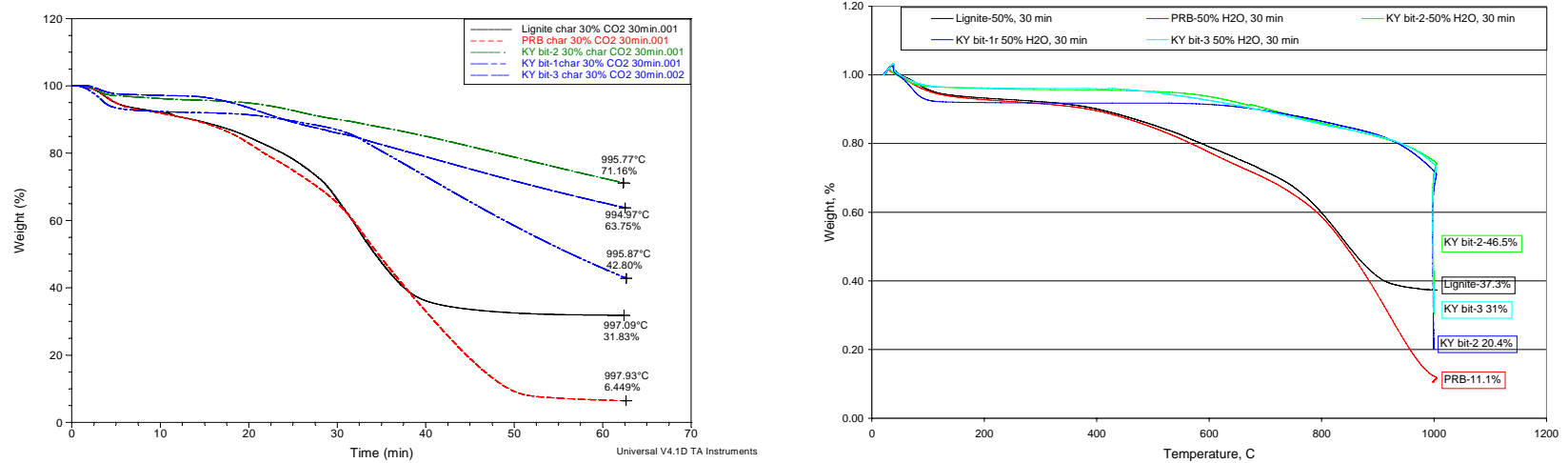


Figure 9-1. Effect of CO<sub>2</sub> concentrations on conversion efficiency of Coal Chars

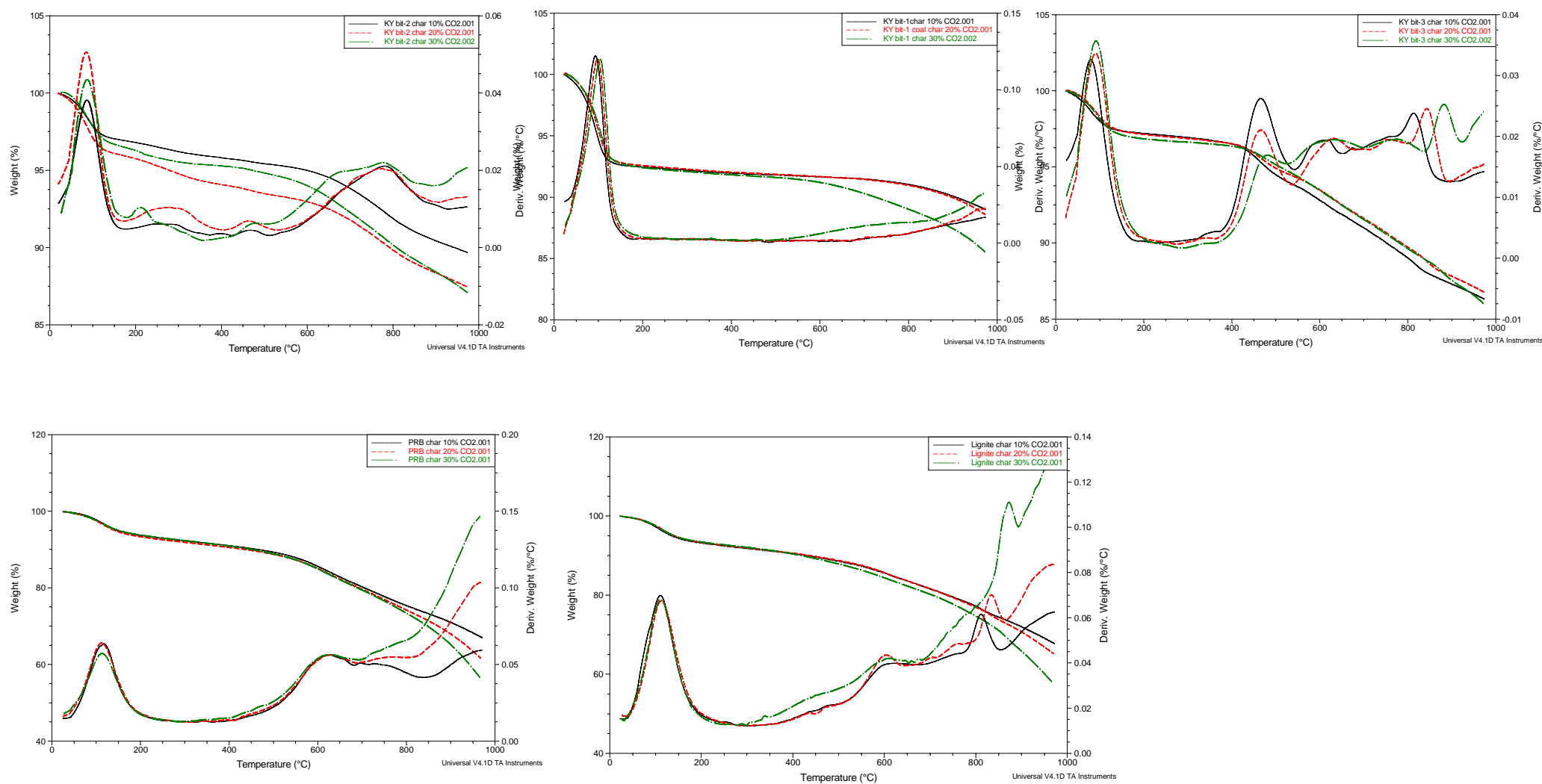


Figure 9-2. Effect of H<sub>2</sub>O concentrations on conversion efficiency of Coal Chars

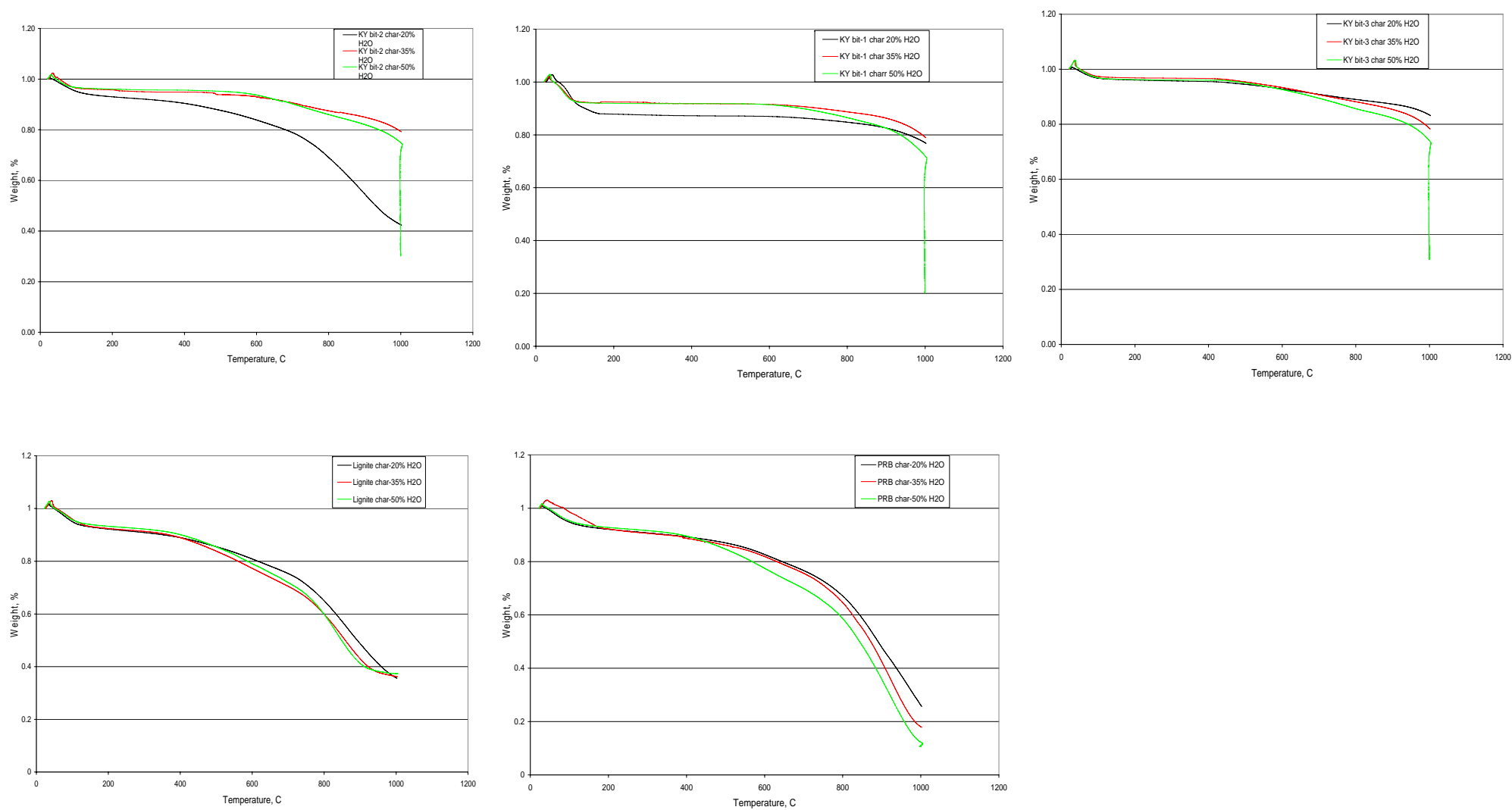
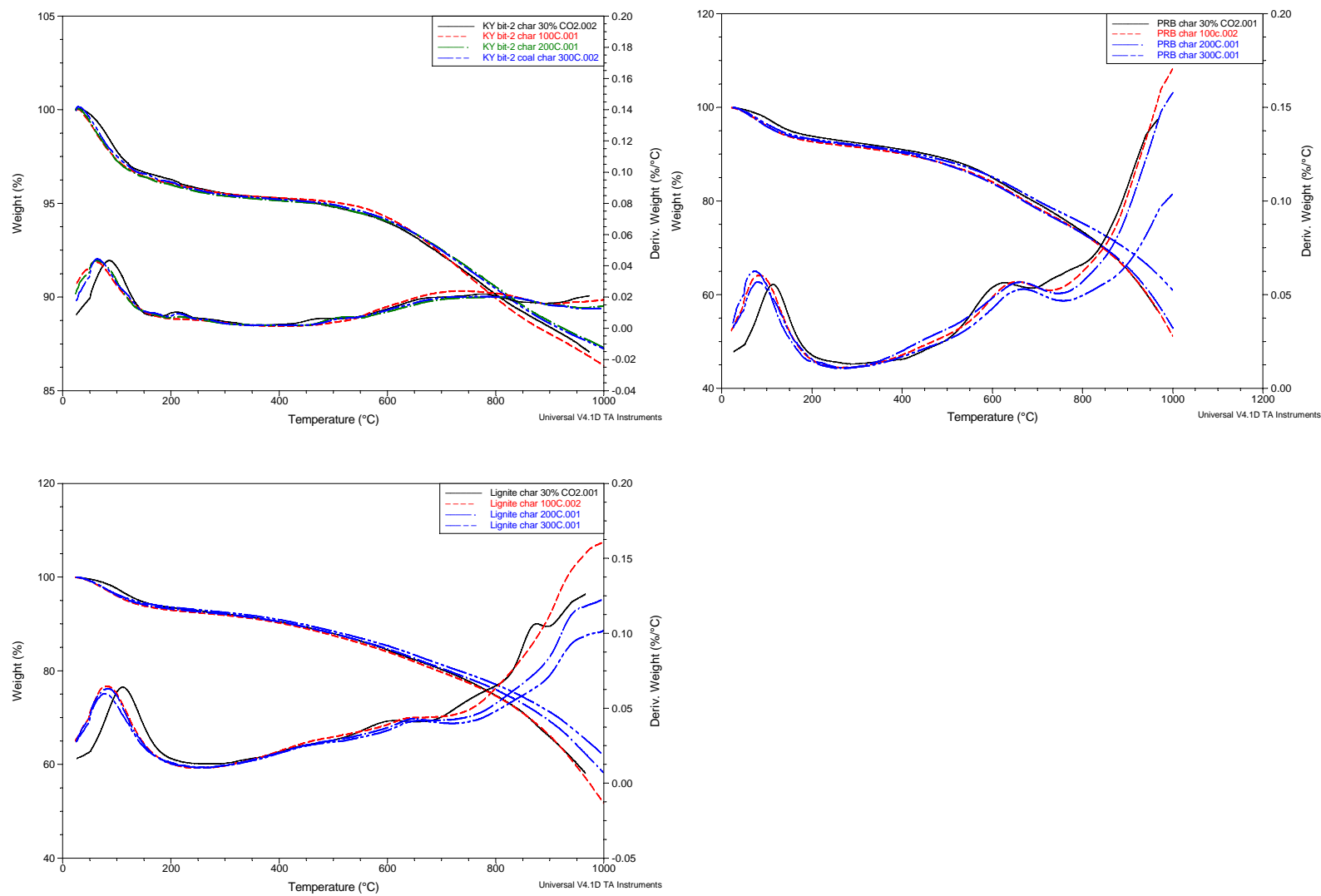


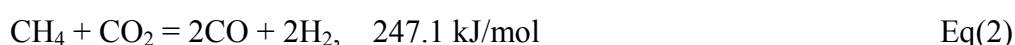
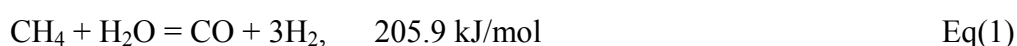


Figure 10. Effects of heating rates on conversion efficiency of Coal Chars



## 4.2 Coal-bed Methane Partial Oxidation and Reforming

**4.2.1 Thermodynamics of Methane Reforming and Partial Oxidation.** Under availability of H<sub>2</sub>O and CO<sub>2</sub>, methane could be reformed to produce H<sub>2</sub> and CO according to the following reactions which are indicated in Eq(1) and Eq(2). These two reactions are so called methane reforming. With a supply of under stoichiometric coefficients of oxygen, methane could be partially oxidized to produce H<sub>2</sub> and CO according to the following reaction, which is indicated in Eq(3). The CO could be further reacted with an excessive supply of H<sub>2</sub>O to produce more H<sub>2</sub>. We call this reaction a water shift reaction, as indicated in Eq(4).



In this study, methane was added in the coal gasification process, in which a mixture of H<sub>2</sub>O, CO<sub>2</sub>, O<sub>2</sub> was available. That means all reactions on CH<sub>4</sub> reforming and partial oxidation, as indicated in Eq(1) through Eq(4), possibly occur. Thermodynamics calculations are conducted in this study to investigate synthesis gas yields and their constituents with varied temperatures and ratios of reforming agents. Calculation ranges of temperatures were 200 °C to 1100 °C at the ambient pressure. The calculation conditions on ratios of reforming agents are shown in Table 2.

Table 2. The Inertial Conditions for Thermodynamic Calculation of CH<sub>4</sub>

Species (mole)	CH <sub>4</sub>	H <sub>2</sub> O	O <sub>2</sub>	CO <sub>2</sub>	CO
1	1	1	0	0	0
2	1	0	0	1	0
3	0	1	0	0	1
4	1	0	0.5	0	0
5	2	2	0	1	1
6	3	2	0.5	1	1

Figure 11 shows thermodynamics calculation results of methane reforming under H<sub>2</sub>O and CO<sub>2</sub> atmospheres, methane partial oxidation under O<sub>2</sub> atmosphere and water shift reaction at the ambient pressure. As indicated in Figure 11-a for the methane steam reforming reaction, the conversion efficiency of methane at the equilibrium status was dependent on temperature. The elevated temperature was favored to increase the methane conversion

efficiency due to the endothermic property of steam reforming of methane. The equilibrium conversion efficiency of methane at 900 °C was 96.4%. The product selectivity under reaction equilibrium status, which is presented as the sum of H<sub>2</sub> and CO, increased with methane conversion efficiency by increasing temperature. Opposite to the trend of methane conversion efficiency and its selectivity under H<sub>2</sub>O atmosphere, its ratio of H<sub>2</sub> and CO decreases as the temperature increases. This ratio was higher at about 23 when the temperature was 500 °C. By increasing the temperature, this ratio gradually decreased until the temperature reached 900 °C, where the ratio of H<sub>2</sub> and CO got close to its stoichiometric ratio of synthesis gas by methane-steam reforming, which was 3. It was interesting to find there were some gas species such as CO<sub>2</sub> in the synthesis gas product, which were not supposed to appear during methane steam reforming, based on the reaction equation, indicated in Eq(1). It seemed some CO was converted into CO<sub>2</sub> in the synthesis gas under low temperature range. This resulted in the higher ratio of H<sub>2</sub> and CO.

As indicated in Figure 11-b, the temperature is also a major impact on the methane conversion efficiency under the CO<sub>2</sub> atmosphere at the equilibrium status. The elevated temperature was favored to increase the conversion of methane due to the endothermic property of CO<sub>2</sub> reforming of methane. The equilibrium conversion efficiency of methane CO<sub>2</sub> reforming was slightly high at 98% when the temperature reached 900 °C. The product selectivity (the sum of H<sub>2</sub> and CO) under reaction equilibrium status increased faster during the temperature increase compared to that of methane steam reforming. Opposite to the trend of conversion efficiency and product selectivity of methane CO<sub>2</sub> reforming, the ratio of H<sub>2</sub> and CO was higher at about 8 when the temperature was 500 °C. Increasing temperature, this ratio gradually decreased until the temperature reached 900 °C, where the ratio of H<sub>2</sub> and CO got close to the stoichiometric ratio of synthesis gas by methane CO<sub>2</sub> reforming, which was 1. There was some H<sub>2</sub>O in the synthesis gas product, which was not supposed to be appear during methane CO<sub>2</sub> reforming based on the reaction equation, which is indicated in Eq(2).

As indicated in Figure 11-c, the conversion efficiency of methane increased with an increase of temperature under an O<sub>2</sub> atmosphere. The equilibrium methane conversion efficiency of the partial oxidation by O<sub>2</sub> was about 98.1% when the temperature reached 900 °C. The product selectivity (the sum of H<sub>2</sub> and CO) under reaction equilibrium status increased mainly due to increases of methane conversion efficiency by the increase of temperature. Opposite to the trend of conversion efficiency and product selectivity of methane partial oxidation by O<sub>2</sub>, a temperature increase will result in the decrease of the ratio of H<sub>2</sub> and CO. Until 900 °C, the ratio of H<sub>2</sub> and CO was close to the stoichiometric ratio of

synthesis gas by methane partial oxidation by  $O_2$ , which was 2. During the partial oxidation of  $CH_4$  by  $O_2$ , both  $H_2O$  and  $CO_2$  were available in the synthesis gas product, which were not supposed to be appear in methane partial oxidation by  $O_2$  based on the reaction equation in Eq(2).

As discussed in the previous three paragraphs on reforming and partial oxidation of methane, high ratios of  $H_2$  and  $CO$  were found under their thermodynamic equilibrium when temperatures were below about  $600\text{ }^\circ\text{C}$ , which were far greater than the stoichiometric factors of synthesis gas products. They resulted from the interference of the water shift reaction as indicated in Eq(4), which correlates with three major species including:  $H_2$ ,  $H_2O$ ,  $CO$  and  $CO_2$ . Under a low temperature range (below about  $700\text{ }^\circ\text{C}$ ), the water shift reaction (Eq(4)) was thermodynamically favored to generate  $H_2$  by consuming?  $CO$ , by which the ratio of  $H_2$  and  $CO$  is much higher. The interference of the water shift reaction was be eliminated as the temperature increased to about  $600\text{ }^\circ\text{C}$  and above. As the temperature increased to an even higher level, such as above  $850\text{ }^\circ\text{C}$ , the reverse of the water shift reaction occurred. Both  $H_2$  and  $CO_2$  started to decrease and  $CO$  and  $H_2O$  increased.

In this study, we only focused on four reactions, which were indicated in Eq(1) through Eq(4) under a temperature window of  $900\text{ }^\circ\text{C}$  to  $1000\text{ }^\circ\text{C}$ . At this temperature window, thermodynamic calculations indicate that both the conversion efficiency of  $CH_4$  and the reaction selectivity of the produced synthesis gas (the sum of  $H_2$  and  $CO$ ) could achieve above 100%. All ratios of  $H_2$  ad  $CO$  reach their chemical stoichiometric factors. In actual situations, there is no distinct boundary between four reactions and all species are available in the synthesis gas production, which will result in very complicated interferences between these reactions. The thermodynamics of  $H_2O$  and  $CO_2$  or the thermodynamics of  $H_2O$ ,  $CO_2$  and  $O_2$  are shown in Figure 12. Figure 12 indicates that these two systems do not make much difference on three critical parameters of synthesis gas. Temperature is a major factor in controlling  $CH_4$  conversion efficiency and  $(H_2+CO)$  selectivity. At temperatures between  $900\text{ }^\circ\text{C}$  to  $1000\text{ }^\circ\text{C}$ ,  $CH_4$  conversion efficiency and  $(H_2+CO)$  selectivity is above 90%. The generation of  $H_2O$  and  $CO_2$  in synthesis gas results in the loss of some of selectivity. However, the  $H_2/CO$  ratio is only about 1.4. The decrease of temperature will result in increases of  $H_2/CO$  ratio in synthesis, but  $CH_4$  conversion and  $(H_2+CO)$  selectivity will also decrease.

Figure 11-1 Thermodynamics of methane reforming ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ), methane partial oxidation ( $\text{O}_2$ ) and water shift reaction under ambient pressure

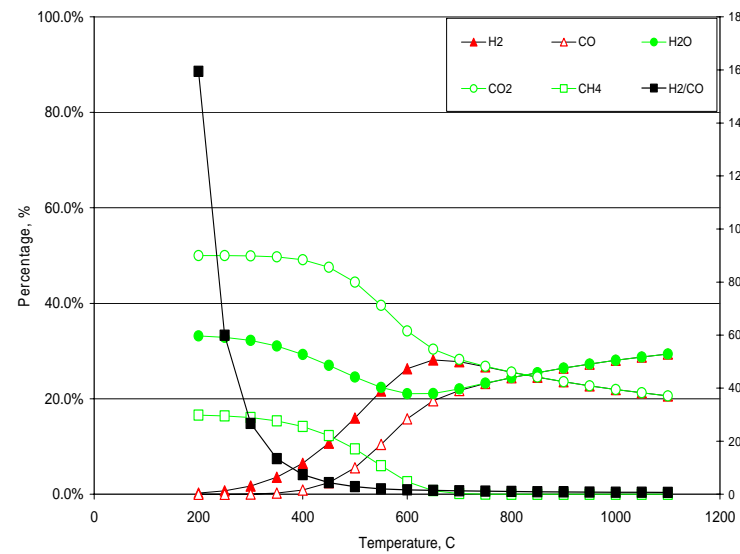
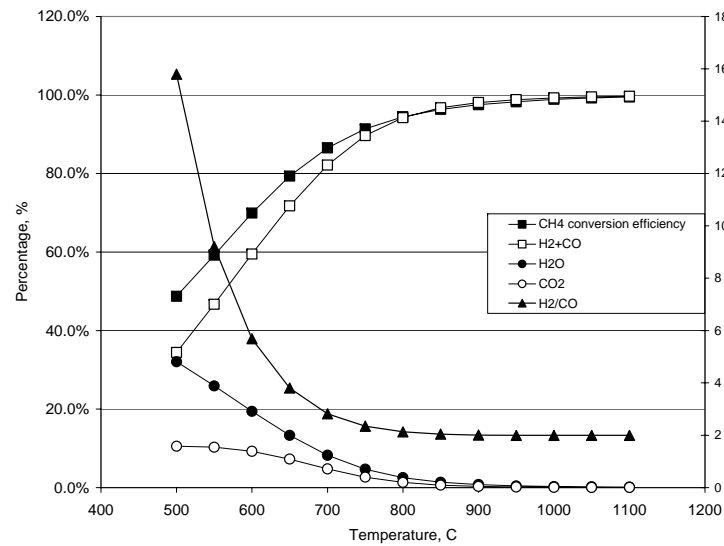
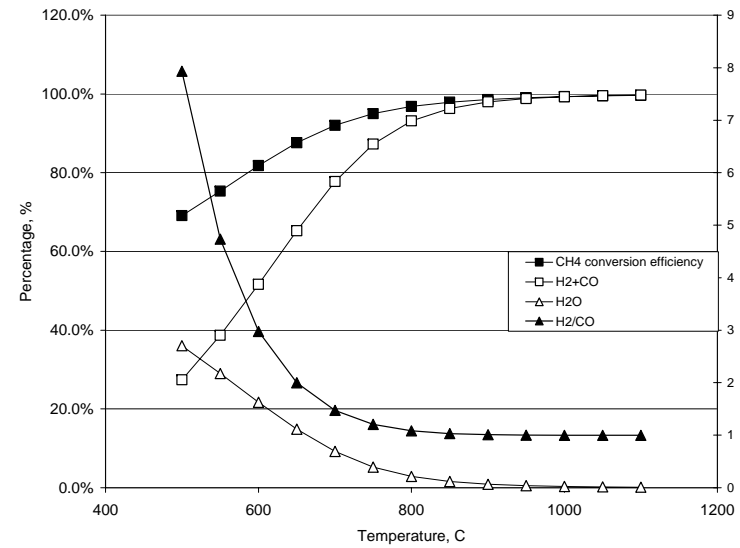
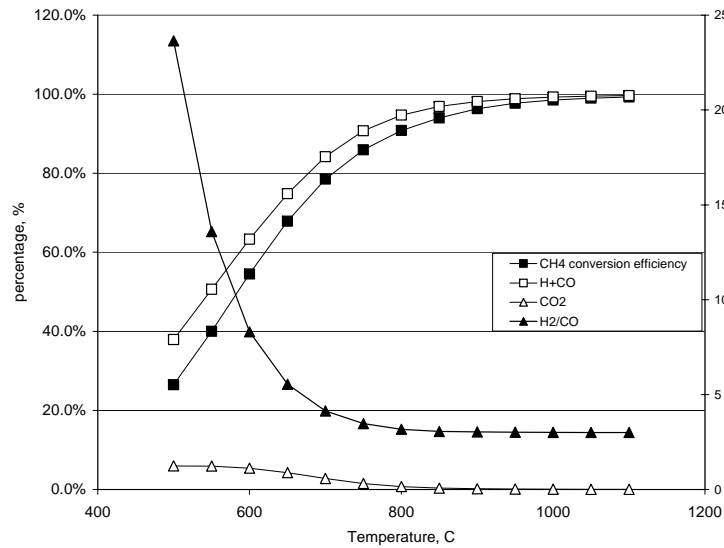
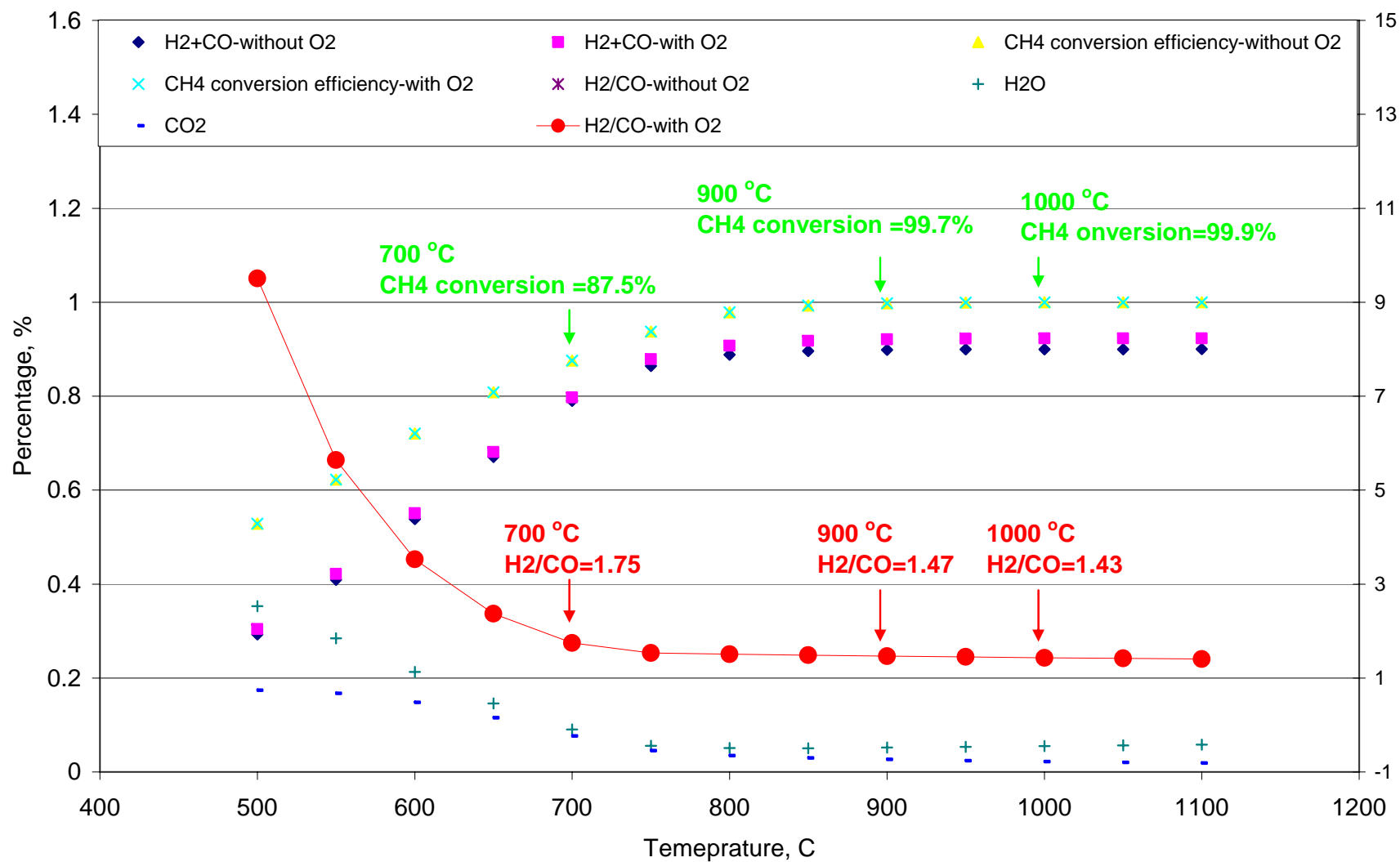


Figure 12. Thermodynamics of methane reforming ( $\text{H}_2\text{O}$  and  $\text{CO}_2$ , without  $\text{O}_2$ ) and methane reforming and partial oxidation ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$  with  $\text{O}_2$ ) under ambient pressure



#### 4.2.2 Test Results.

Thermodynamics calculation indicates there is no major limitation on occurrence of the methane steam reforming if the temperature is above 700 °C, as indicated in Figure 11. Thus, the conversion efficiency of methane and its selectivity are solely dependent on its kinetics. Commercially, methane steam reforming needs a catalyst to promote the reaction kinetics. The most popular commercial catalyst for methane steam reforming is NiO with its larger specific surface areas. In this study, the kinetics of methane reforming and partial oxidation was evaluated in a 1" test rig. Catalytic effects of coal chars and fly ashes from gasification processing on methane steam reforming were evaluated. CH<sub>4</sub> conversion efficiency, selectivity and the ratio of H<sub>2</sub> and CO of methane steam reforming by different coal chars and fly ashes are shown in Figure 13-1 through 13-3, respectively. Blank test is conducted to compare the catalytic effects of different coal chars and fly ashes on methane steam reforming. PRB ACC1 and Lignite ACC1 are gasification chars derived from low rank coals, for which the specific surface areas are higher at 649.3 m<sup>2</sup>/g and 359.9 m<sup>2</sup>/g, respectively. KY bit-3 SCC is carbonization char from the pyrolysis process with a lower specific surface area at 3.03 m<sup>3</sup>/g. Two commercial gasification chars are from commercial IGCC processes. Their specific surface areas are lower since they become slag after higher temperature treatment in the gasifier.

As indicated in Figure 13-1(a), the temperature is a major factor in CH<sub>4</sub> conversion efficiency. The increase of CH<sub>4</sub> conversion efficiency is nearly 25 % by the temperature increase from 700 °C to 900 °C for Lignite ACC1. CH<sub>4</sub> conversion efficiencies by coal chars are all greater than that in the blank test, which confirms the occurrence of catalytic effects by coal chars. It seems coal char with higher specific surface area, such as PRB ACC1 and Lignite ACC1, result in higher CH<sub>4</sub> conversion efficiencies, and carbonization char and commercial chars result in lower CH<sub>4</sub> conversion efficiencies, which are comparable to that in the blank test. It was also found (Figure 13-1(b) and 13-1(c)) that there is a greater catalytic effect on methane steam reforming by coal chars than by fly ashes, which are derived from same coals. Similarly, the specific surface areas of coal chars are generally higher than those of fly ashes, which is one of the possible reasons to explain the difference of catalytic effect by coal chars and fly ashes.

The selectivity of methane steam reforming, as presented by the sum of H<sub>2</sub> and CO, is shown in Figure 13-2. Similarly, the temperature is a major factor on the selectivity of methane steam reforming. The increase of selectivity of methane steam reforming is nearly 35 % by the temperature increase from 700 °C to 900 °C for Lignite ACC1. The selectivity

also increases with increases of the specific surface area of coal chars. However, the variation of selectivity is not greater by variation of the specific surface area than that by the temperature variation. The selectivity of coal chars is also greater than that of fly ashes, possibly due to the same reasons as that of CH<sub>4</sub> conversion efficiency, which are indicated in Figure 13-2(b) and Figure 13-2(c). This trend is apparent in higher temperatures (900 °C) than in lower temperatures (700 °C).



The ratios of H<sub>2</sub> and CO of methane steam reforming by different coal chars and fly ashes are shown in Figure 13-3. Temperature seems to be negatively correlative to the ratio of H<sub>2</sub> and CO for both coal chars and fly ashes. Two reactions may impact this ratio during methane steam reforming. Under the lower temperature range, the ratio of H<sub>2</sub> and CO increase by generating H<sub>2</sub> and consumption of CO by the water shift reaction. Under a higher temperature range, the methane decomposition reaction, as indicated in Eq(5), could increase H<sub>2</sub> concentrations in the produced synthesis gas despite the restriction of the water shift reaction. The confirmation of methane decomposition reaction could be confirmed in tests of both the 1" test rig and followed by the 2.5" gasification demonstration units since soot is found in the synthesis gas in some test runs. Due to the interference of the methane decomposition reaction, the ratio of H<sub>2</sub> and CO is generally larger than that of stoichiometric factors of Eq(1). Although the higher ratio of H<sub>2</sub> and CO is expected for the co-gasification process, the soot produced is not expected since it's difficult to be burnout.

As indicated in Figure 13-4, steam supply with RSM (the ratio of steam and methane) at 2 and 3, which are higher than the stoichiometric factor, does not help on the abatement of soot formation at 900 °C since the ratio of H<sub>2</sub> and CO are still higher than stoichiometric factors of the synthesis gas product in Eq(1). As expected, the increase of RSM does increase the CH<sub>4</sub> conversion efficiency and selectivity in this study since methane steam reforming is a process with kinetics control. Higher partial pressure of steam will increase process kinetics. However, this impact is limited. Due to energy penalties, we do not suggest a higher steam ration which is applied in methane steam reforming processes. Figure 13-5 shows the impact of variations of the space velocity on CH<sub>4</sub> conversion efficiency, selectivity and the ratio of H<sub>2</sub> and CO during the methane reforming process. The increases of the space velocity will result in the decrease of the CH<sub>4</sub> conversion efficiency. Similarity is found for the trend of selectivity. At temperatures above 900 °C, the variation of the space velocity does not impact the ratio of H<sub>2</sub> and CO.

The investigation of methane CO<sub>2</sub> reforming by variation of RCM (the ratio of CO<sub>2</sub> and



methane) is shown in Figure 14. As indicated in Figure 14(a), the selectivity increases by increasing RCM. It seems that higher RCM increase the kinetics of methane CO<sub>2</sub> reforming. However, this impact is limited and could not be compared to the impact of temperature. Temperature should be the most significant positive impact factor on methane CO<sub>2</sub> reforming. From Figure 14(b), it can also be found that the content of CO is higher than that of H<sub>2</sub> at high RCM and bed temperatures. The reverse of the water shift reaction (Eq(6)) is also an endothermic reaction, which is favored at the high temperature. The outcome of this reaction makes the concentration of CO increase in the synthesis gas and the concentration of H<sub>2</sub> decrease. The increase of RCM means more carbon dioxide entering into the reactor to participate in the reaction, which can increase the partial pressure of CO<sub>2</sub> and thus make reactions faster to generate the concentration of CO and decrease the concentration of H<sub>2</sub>.



Figures 15 and 16 show the effects of temperature, space velocity, and ROM (ratio of oxygen to methane) on three parameters (CH<sub>4</sub> conversion efficiency, selectivity and the ratio of H<sub>2</sub> and CO) of methane partial oxidation. At the constant space velocity and ROM, all three parameters increase when the bed temperature increases from 700 °C to 900 °C. However, the ratio of H<sub>2</sub> and CO is always less than 1 as indicated in Figure 15. At the constant bed temperature and ROM, all three parameters just slightly increase with the space velocity increase. This may indicate the fast kinetics of CH<sub>4</sub> partial oxidation. At the constant temperature and space velocity, the decrease of ROM from 1/2 to 1/3 leads to a little rise of selectivity in produced gas during methane partial oxidation. It could be seen that the methane conversion increases with the increase of ROM, while the ratio of H<sub>2</sub> and CO and the sum of H<sub>2</sub> and CO have a reverse change rule above 900 °C. The high ROM means more oxygen will participate in the reaction of methane's direct or partial oxidation and more methane will be consumed during methane's direct or partial oxidation. The increase of oxygen may burnout CO and H<sub>2</sub> into CO<sub>2</sub> and H<sub>2</sub>O, which will reduce the content of CO and H<sub>2</sub> in produced gas. Simultaneously, the high ROM means more nitrogen is available in synthesis gas, which dilutes the concentrations of H<sub>2</sub> and CO. Since the adjustability of methane's partial oxidation by oxygen is not idealistic and there is a possibility that it could consume H<sub>2</sub> and CO, injecting CH<sub>4</sub> in the co-gasification process should select zone where oxygen is not available for CH<sub>4</sub> burnout or partial oxidation.

Figure 13-1. Steam methane reforming by different coal chars and fly ashes

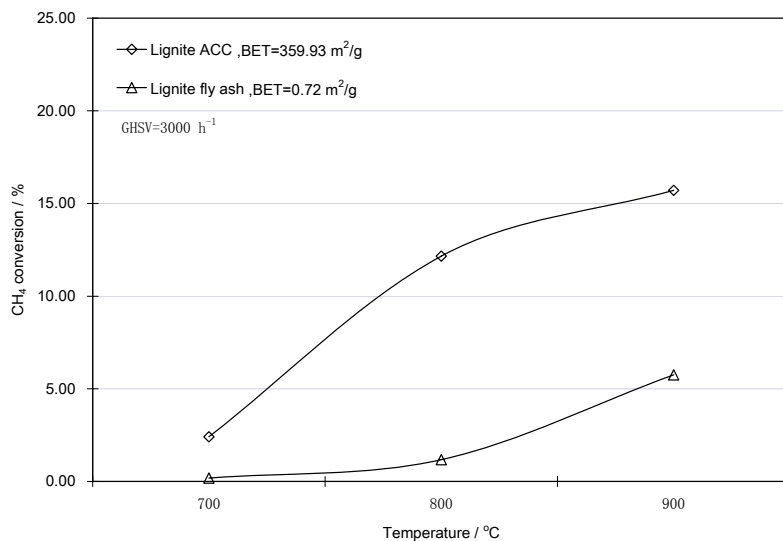
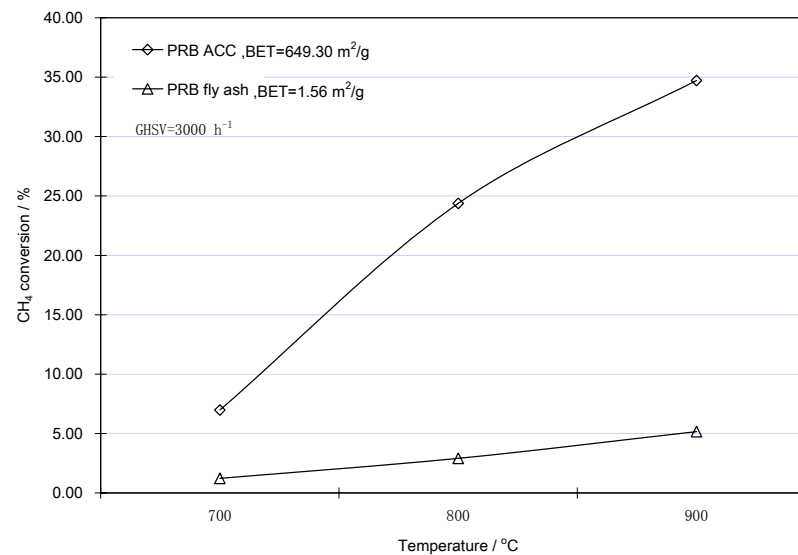
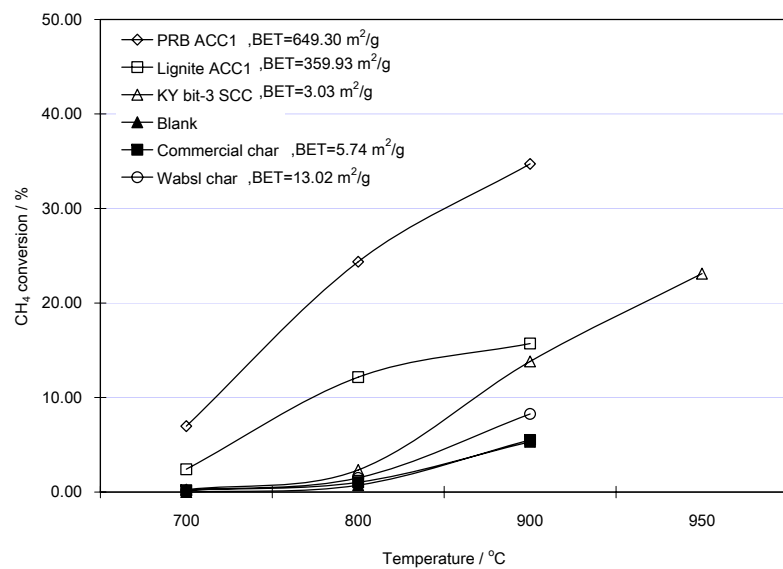


Figure 13-2. ( $H_2+CO$ ) selectivity of steam methane reforming by different coal chars and fly ashes

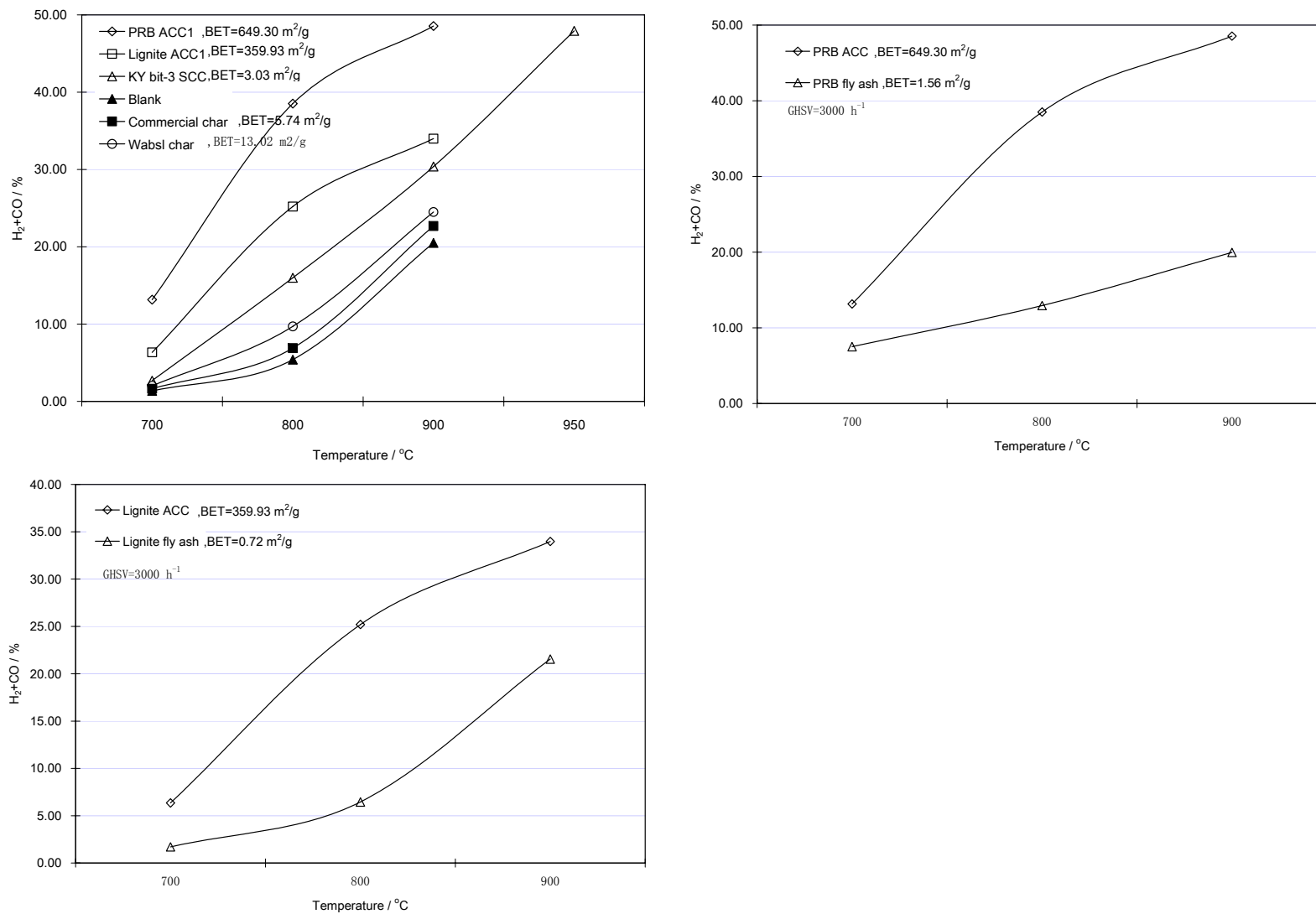


Figure 13-3. The ratio of  $H_2/CO$  of steam methane reforming by different coal chars and fly ashes

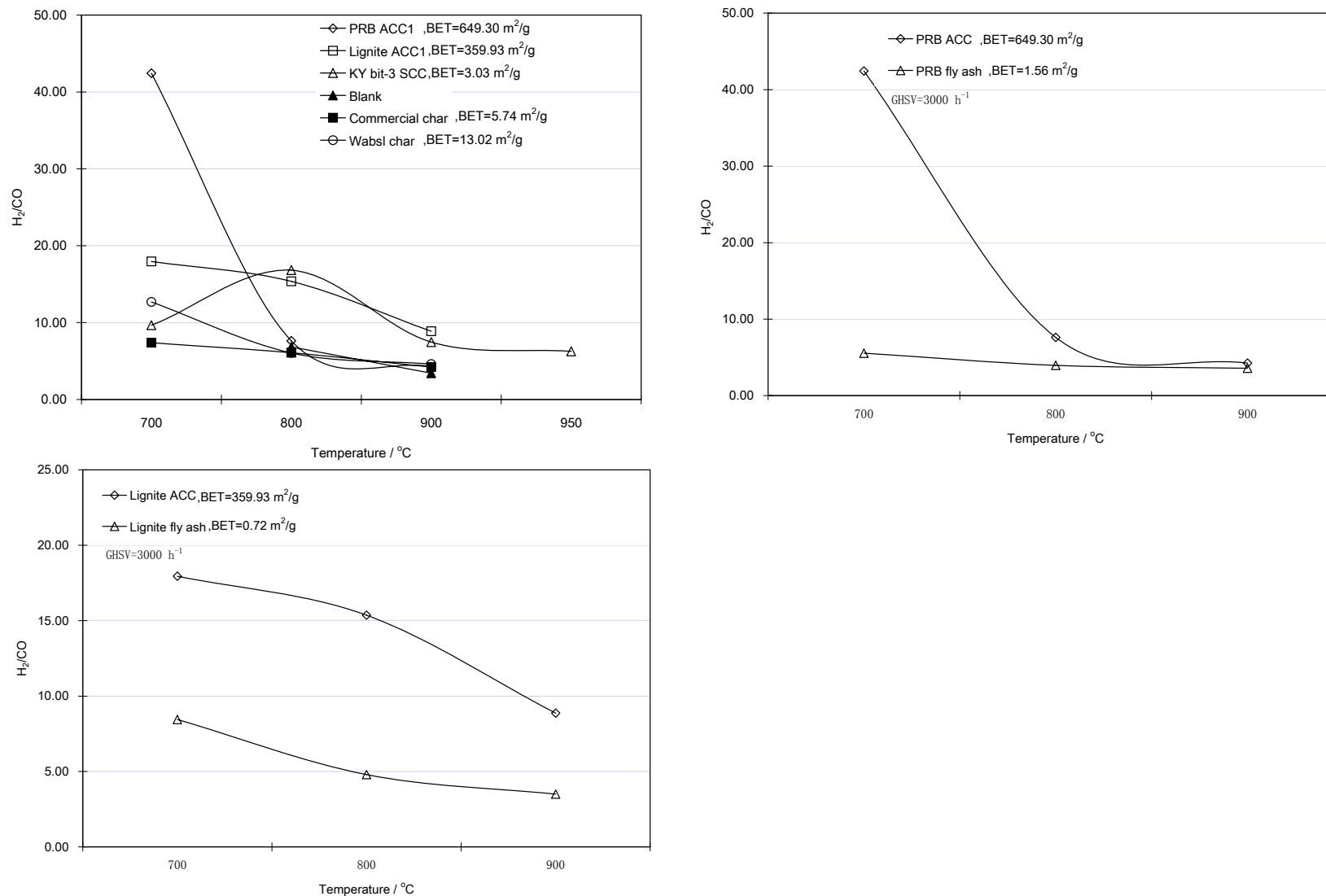


Figure 13-4. Effects of RSM on CH<sub>4</sub> conversion efficiency, selectivity and the ratio of H<sub>2</sub>/CO under steam methane reforming by KY bit-3 chars

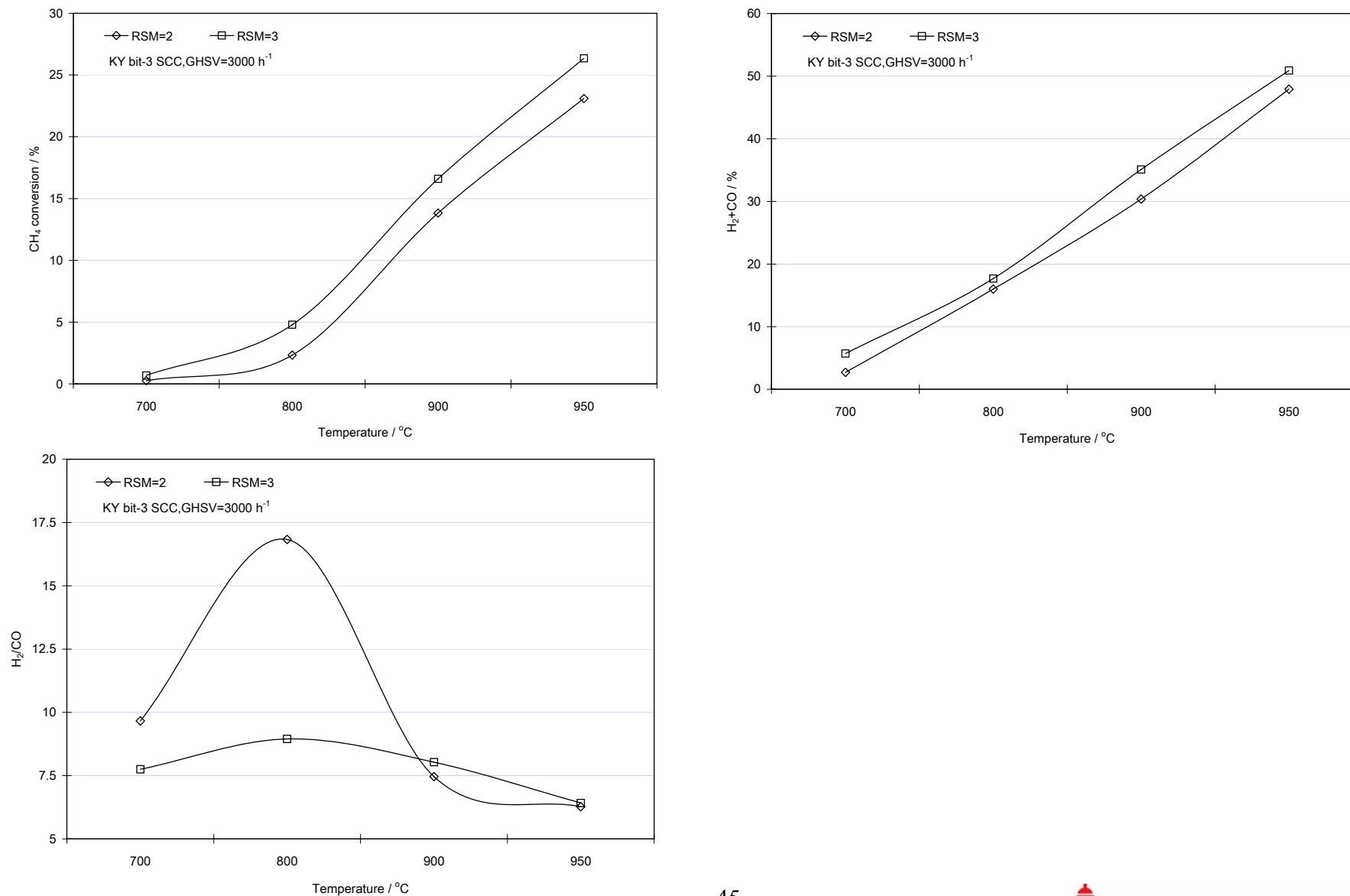


Figure 13-5. Effects of SV on CH<sub>4</sub> conversion efficiency, selectivity and the ratio of H<sub>2</sub>/CO under steam methane reforming by KY bit-3 chars

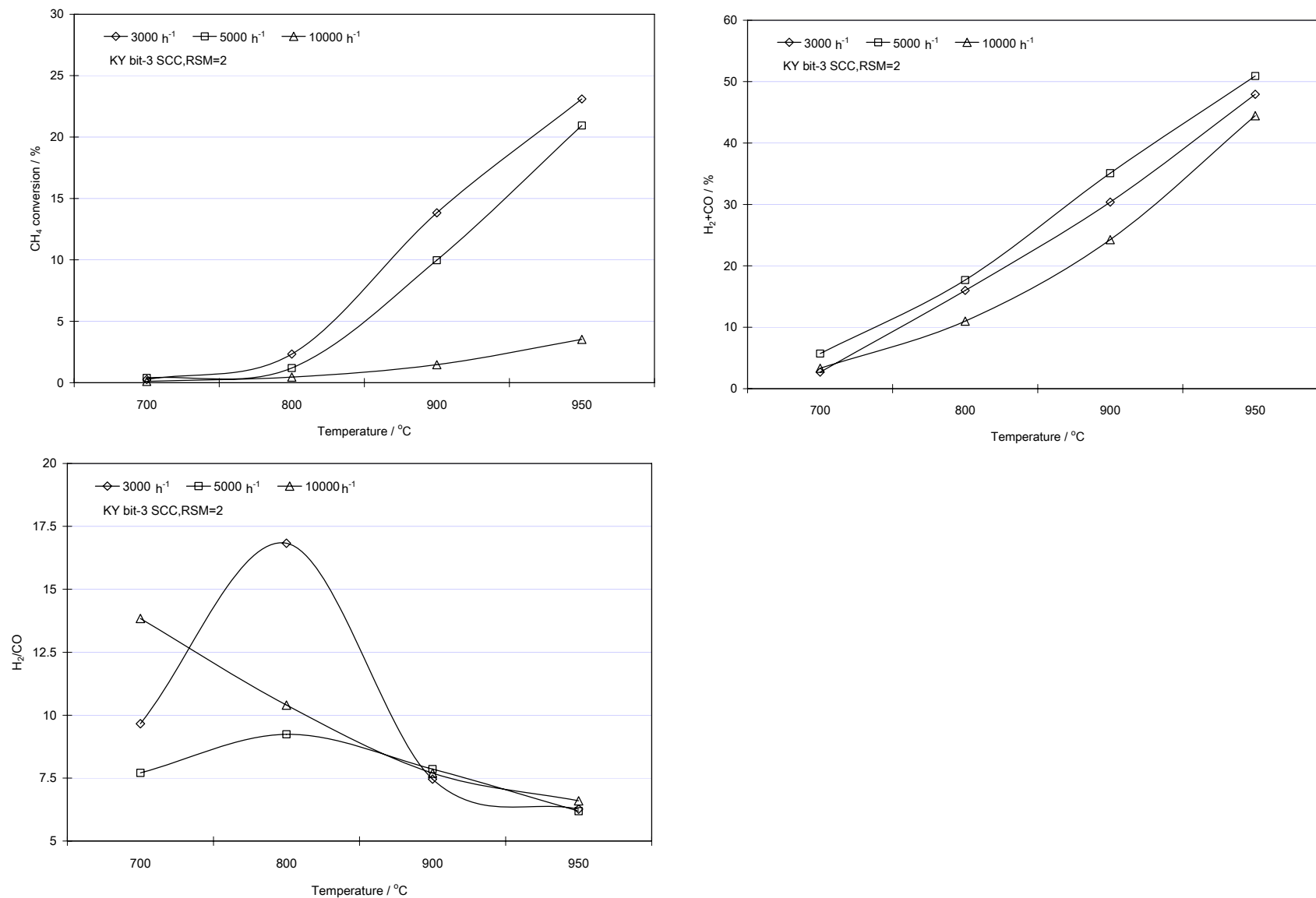


Figure 14. Effects of RCM on selectivity and the ratio of  $H_2/CO$  under  $CO_2$  methane reforming by KY bit-3 char

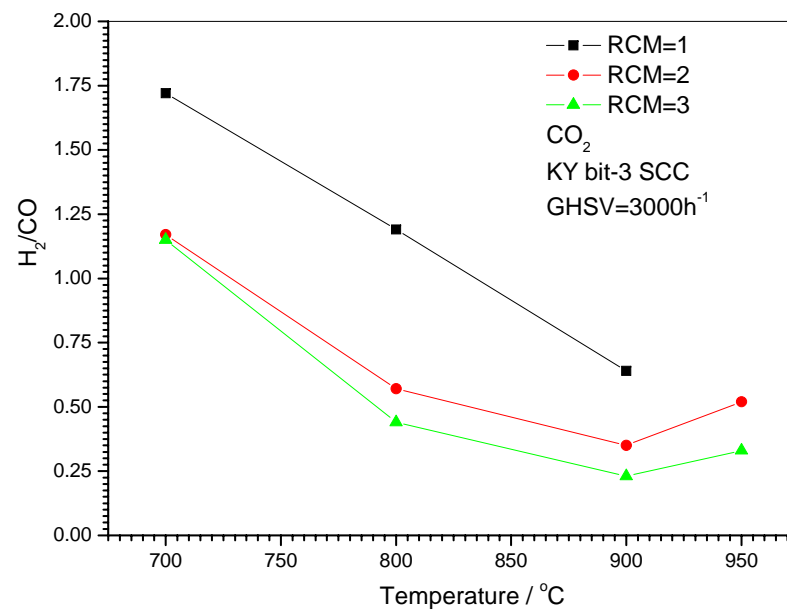
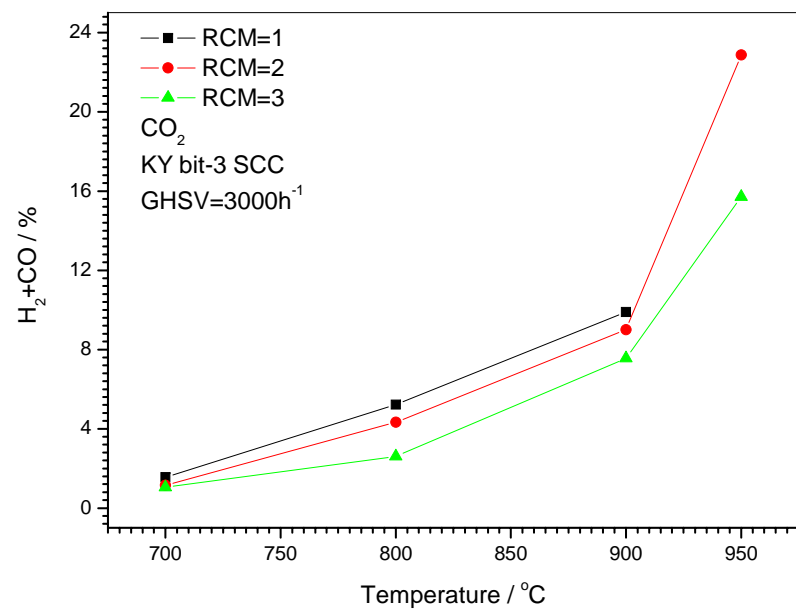




Figure 15. Effects of space velocity on methane partial oxidation by O<sub>2</sub>

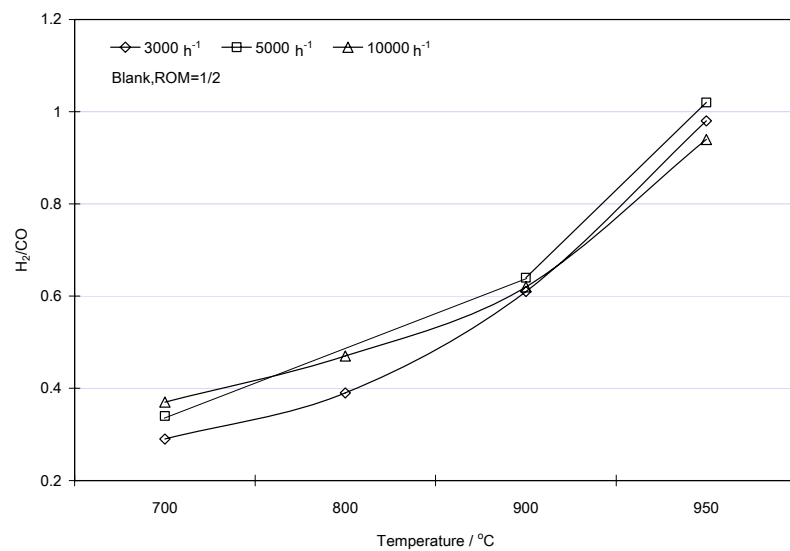
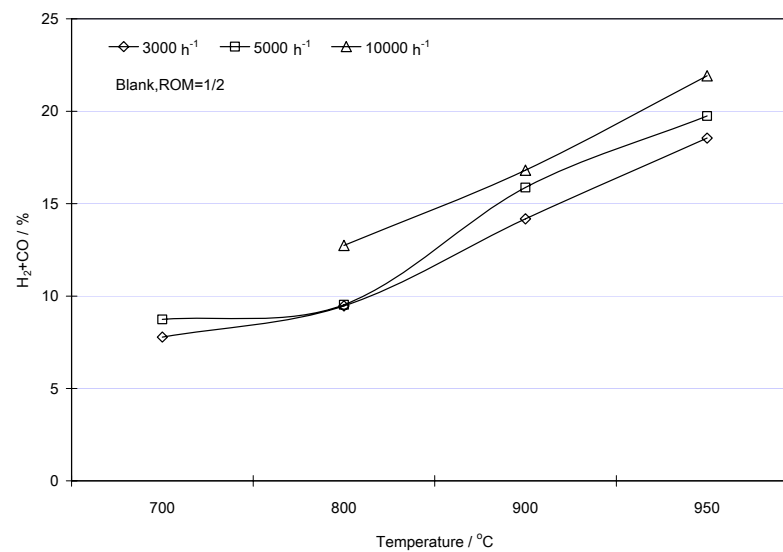
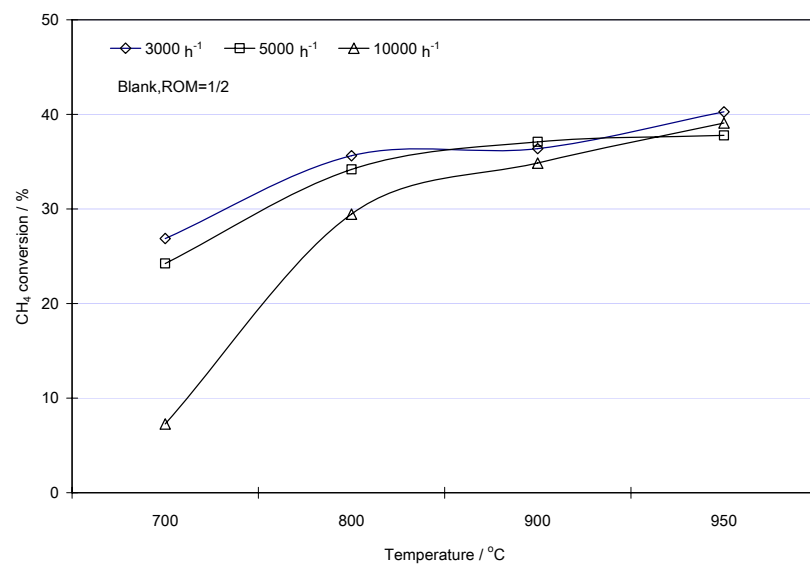
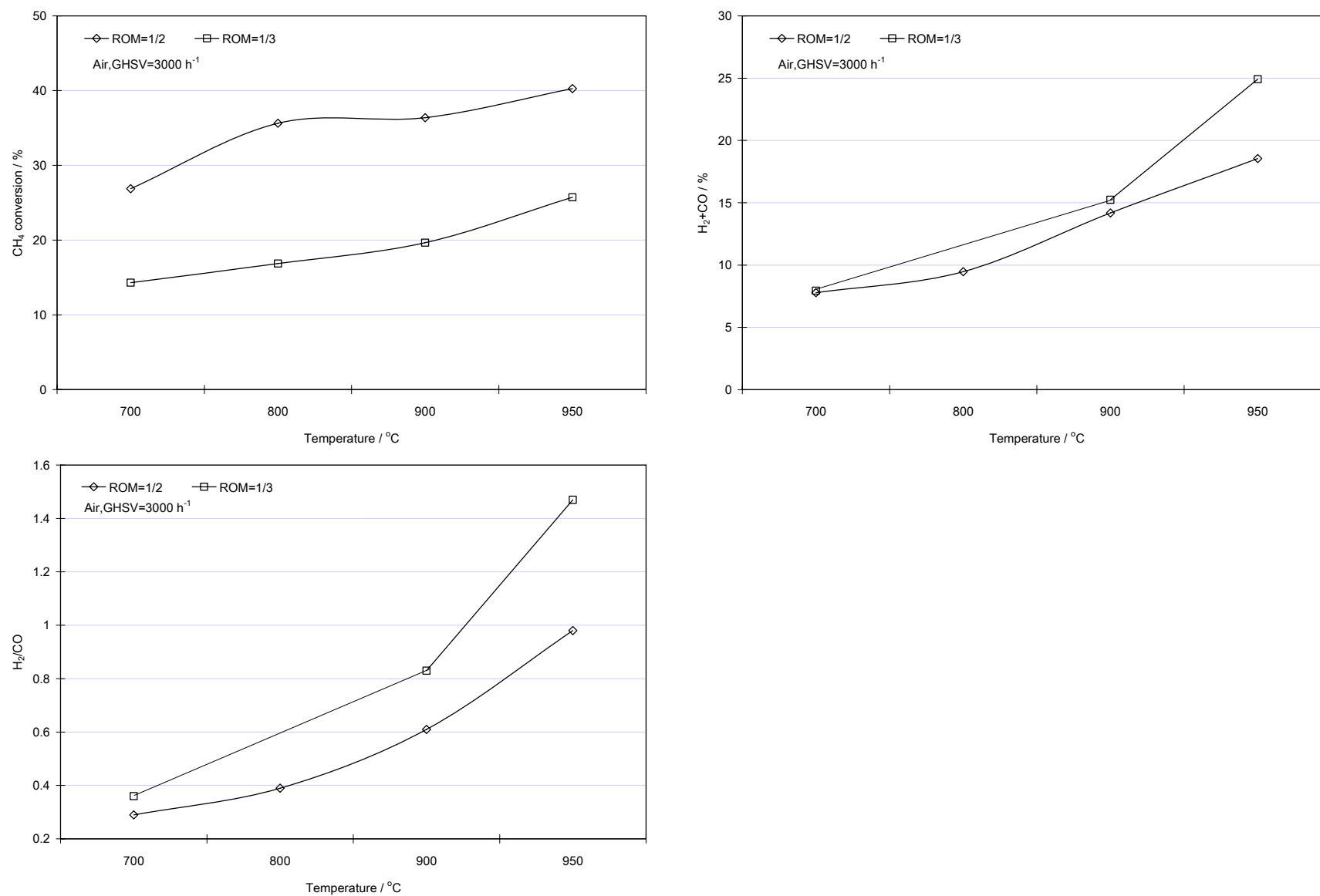
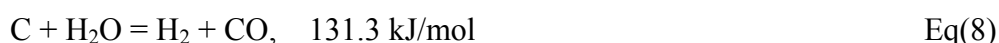


Figure 16. Effects of RCM on methane partial oxidation by O<sub>2</sub>



### 4.3 Heat and Mass Balance

Several reactions occur in the coal gasification process. Coal is firstly pyrolyzed and generates  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$  and  $\text{H}_2\text{O}$  (coal pyrolysis) at the elevated temperature. The partial  $\text{CH}_4$  and coal char, which are produced in the pyrolysis process, will be consumed by the supplied air or oxygen to generate  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (oxidation). The majority of the pyrolysis char will react with supplied or generated  $\text{H}_2\text{O}$  to produce  $\text{H}_2$  and  $\text{CO}$  in the followed-up char  $\text{H}_2\text{O}$  gasification process, in which the produced  $\text{CO}_2$  in the oxidation process possibly involves into the char gasification process to produce  $\text{CO}$  (char  $\text{CO}_2$  gasification). The water shift reaction (Eq(4)) is not favored in the high temperature coal gasification process because the general operational temperature is higher than  $900^\circ\text{C}$ . If the coal gasification process is autothermic, the total enthalpy, which is released in the coal combustion process (exothermic reaction), must be equal to the total enthalpy that is needed in the coal gasification process (endothermic reaction). The endothermic enthalpy of the coal pyrolysis process can be ignored because it is much smaller than that in the char gasification process. Char gasification by  $\text{CO}_2$  has less reactivity than that by  $\text{H}_2\text{O}$ . Therefore, two basic reactions, as indicated in Eq(7) and Eq(8), can be simply and reasonably describe the coal gasification process. To achieve the gasification process the autothermic, the enthalpy of exothermic reaction of Eq(7) should be equal to the enthalpy of the endothermic reaction of Eq(8). Based on these criteria, the gasification of  $\frac{3}{4}$  carbon in mass in the gasification process by  $\text{H}_2\text{O}$  should consume  $\frac{1}{4}$  of the carbon in mass to achieve heat balance of the autothermic coal gasification process. Thus, mass balance could be built up and compositions and gas yield of synthesis gas could be predicted under these theoretical calculation conditions. In this calculation, H in coal is totally converted into  $\text{H}_2$  and there is no  $\text{CH}_4$  generation and  $\text{O}_2$  left in this synthesis gas.



The theoretical operational conditions and predictions of compositions and gas yield of synthesis gas are shown in Table 3-1. It includes two possible operational modes in this study, the oxygen-blown mode, and the air-blown mode. Three typical U.S. coals with different ranks are considered. Only KY bit-2 coal is considered in this calculation because the other two tested Kentucky coals have similar proximate and elemental analysis. It was indicated that the ratio of air (oxygen) and coal and the ratio of steam and coal increase with the increases of coal ranks due to the increasing of coal carbon content. The ratios of air and coal in  $\text{NM}^3/\text{kg}$ , in sequence of increasing coal ranks, are 0.68 for Lignite, 1.38 for PRB Sub-bituminous coal and 1.57 for Kentucky Bituminous coals. Meanwhile, the ratio of steam

and coal in kg/kg, in sequence of increasing coal ranks, is 0.41, 0.698 and 0.797, respectively. The air-blown mode generally results in the lower total percentage of  $H_2$  and CO because of heat loss carried by the inert  $N_2$  steam and higher synthesis production because of the dilution effect of  $N_2$  in the air supply. However, it does not affect the ratio of  $H_2$  and CO, which is generally higher than 1. They were not largely dependent on the operational modes (the air-blown or the oxygen-blown), but largely dependent on the coal ranks. The total percentage of  $H_2$  and CO is about 60% at air-blown mode and above 88% at oxygen mode for all tested coals. Both coal ranks and carbon conversion efficiency affect the compositions and yield of synthesis gas production by variation of actual conversion of carbon in coal. The hydrogen in coal does not have much impact on the coal gasification process.

In actual gasification process, more heat loss generally occurs. The possible heat loss should be considered, such as a chemical energy loss of unburned carbon at about 10 % (carbon conversion efficiency at about 90 %), a system heat loss at about 5 %, an apparent heat loss being carried by synthesis gas and emitted ash at about 5 % and an apparent heat loss to generate the water vapor at 5 %. All these itemized heat losses should be supplied by the consumption of partial coal carbon in its oxidation process. That means the previous defined participations of  $\frac{1}{4}$  carbon in the oxidation process and  $\frac{3}{4}$  carbon in the gasification process might be changed to correlation of  $\frac{2}{5}$  carbon in the oxidation process and  $\frac{3}{5}$  carbon in the gasification process. Based on this consideration, the ratios of air and coal in  $NM^3/kg$ , are all increased since more air or oxygen is required. In sequence of increasing coal ranks, the ratios of air and coal were 1.1 for Lignite, 2.2 for PRB Sub-bituminous coal and 2.5 for Kentucky Bituminous coals under air-blown mode. Under oxygen-blown mode, the ratios of oxygen and coal, in  $NM^3/kg$ , were 0.53 for Kentucky Bituminous coal, 0.46 for Wyoming sub-bituminous coal and 0.23 for Lignite. The calculated synthesis gas yield was found to be enlarged consequently with more  $N_2$  in the synthesis gas which was carried in by air. The total percentage of  $H_2$  and CO in the synthesis gas slightly decreased. The ratio of  $H_2$  and CO is increased because of decrease of CO concentration in the synthesis gas, especially for those low rank coals such as lignite. Its ratio of  $H_2$  and CO was about 2.4 for both operational modes. For high rank Kentucky coals, the ratios of  $H_2$  and CO were increased to about 1.7 with comparison to those without consideration of heat loss. However, they are still lower than 2 which was request to be feedstock of chemical synthesis process. Thus, the adjustment of the ratio of  $H_2$  and CO is most likely applied in by the co-gasification process of Kentucky coals.

#### 4.4. Coal Gasification Test in a 2.5" Gasification Demonstration Unit.

Actual operational conditions and test results were shown in Table 4-1 through 4-3 for four tested coals. It could be found in these actual operation conditions for all four tested coals, the air/coal ratio was generally higher than theoretical values at the same carbon conversion efficiency, which was indicated in Table 3-1. The reason was that the heat loss of the gasification system should be considered under the autothermic operation criteria, as indicated in Table 3-2. In this study, we ignored all these heat losses, which were reimbursed by the electric-powered furnace. Thus, the steam/coal ratios were usually set to be same as those in their theoretical calculation. The selection of particle size in the gasifier maintains the fluidization of coal char. Higher temperatures, which were about 950 °C to 1050 °C, were usually applied in operational conditions to maintain higher reactivity of coal char during its gasification. In this study, the operation pressure was at ambient condition. Figure 4-1 showed the correlation between test results with their operation conditions during tests for the KY bit-1 in the 2.5" gasification demonstration unit. For the first three runs with Test Number as 1, 2 and 3, the raw KY bit-1 after pulverization were used. It was found that the fast release of pyrolysis gas in a larger amount and the followed-up char agglomeration make the feeding of this kind of Kentucky coal very difficult in the 2.5" gasification demonstration unit. This issue occurred for all Kentucky Bituminous coals. The outcomes made reactions inside the gasifier to be the coal pyrolysis process in shorter term and followed by the jam of coal feeder. The normal coal gasification process could not be organized. During this period, compositions of synthesis gas were largely varied. The  $H_2/CO$  ratio was generally greater than 2. The carbon conversion was just 35% through 40%.  $CH_4$  content was higher than that of the general occurrence in the coal gasification process.

After several trials and errors, we found the correct method is the pre-treatment of raw KY bit-1 before using it as a feedstock coal. It seemed that the pre-treatment by the pre-oxidation procedures worked for all Kentucky Bituminous coals in this study. Test results with normal gasification operations of KY bit-1 coal were shown in same table with Test Numbers 5, 6 and 7 under the air-blown mode. During the air-blown mode, the ratio of  $H_2/CO$  varied between about 0.9 and 1.2, which was close to its theoretical value of the coal gasification process. The total percentage of  $H_2$  and CO (the cold gas efficiency) in the dry basis varied between about 42% and 45%. The dilution of synthesis gas yield was due to the  $N_2$  in the air, which was used in the air-blown mode. The synthesis production in the dry basis varied between 2.85  $Nm^3/kg$  and 3.31  $NM^3/kg$ , which was lower than its theoretical value at about 3.6  $NM^3/kg$ . The reason that lower carbon conversion efficiency could be achieved

during KY bit-11 gasification was due to its lower gasification reactivity at about 70% in this study. Test results with normal gasification operation of KY bit-1 under the oxygen-blown mode were shown in the same table as Test Numbers 8 and 9. During the oxygen-blown mode, air was replaced by the pure oxygen to be one of the gasification agents. However, the  $N_2$  as a trace element, was used to be fed in the gasifier for purposes of calculation the synthesis gas yield. The ratio of the  $N_2$  addition versus the oxygen supply was about 20%. The additions of tracer  $N_2$  seemed not to impact the coal gasification process under the oxygen-blown mode in this study since the actual  $N_2$  concentration in the produced synthesis gas was only about 3%. Under the oxygen-blown mode, the ratio of  $H_2/CO$  at 0.94 to 1.03 did not change from its theoretical value of about 1 during normal gasification conditions. The total percentage of  $H_2$  and  $CO$  (the cold gas efficiency) in the dry basis was varied between about 73.3% and 75.2%, which was much better than those at air-blown mode conditions. The synthesis gas yield in the dry basis was varied between  $1.87 \text{ Nm}^3/\text{kg}$  and  $1.9 \text{ Nm}^3/\text{kg}$ , which was close but lower than its theoretical value of about  $2.4 \text{ Nm}^3/\text{kg}$ . Lower carbon conversion efficiency, at about 75% in this study, should be responsible for this lower synthesis gas yield.

The same pre-oxidation procedure was applied to the raw KY bit-2 coal before it was fed into the 2.5" gasification unit. It seemed successful on this kind of Kentucky coal after pre-treatment, either. Test results of KY bit-2 were shown in Table 4-2, with Test Numbers 1, 2 and 3 under the air-blown mode and Test Numbers 4 and 5 under the oxygen-blown mode. Under the air-blown mode, the ratio of  $H_2/CO$  was close to its theoretical value (about 1) of the coal gasification process. The total percentage of  $H_2$  and  $CO$  (the cold gas efficiency) on a dry basis was slightly improved at about 48.5%. The synthesis gas production on a dry basis also improved and reached more than  $3 \text{ Nm}^3/\text{kg}$ , although it was still lower than its theoretical value due to incomplete conversion of carbon on coal for KY bit-2. The dilution of synthesis gas yield by  $N_2$  in air was improved by replacing air with pure oxygen under the oxygen-blown mode. We still used tracer  $N_2$  for purpose of the calculation of synthesis production. Under the oxygen-blown mode, the ratio of  $H_2/CO$  was about 1.05, which did not change from its theoretical value of about 1 during normal gasification conditions. The total percentage of  $H_2$  and  $CO$  (the cold gas efficiency) on a dry basis improved to be about 82% on average, which was better than that by gasification of KY bit-1 at the same condition. The synthesis gas yield on a dry basis varied between  $2.012 \text{ Nm}^3/\text{kg}$  and  $2.178 \text{ Nm}^3/\text{kg}$ , which was close but lower than its theoretical value of about  $2.4 \text{ Nm}^3/\text{kg}$ . The improved carbon conversion efficiency for KY bit-2 is responsible for all these improvements.

For comparison purposes, two U.S. coals of low rank with larger productivity were also evaluated in this study. In all, two low rank coals showed pretty good gasification reactivity under both air-blown and oxygen-blown modes. Above 90 % of the carbon conversion efficiency could be achieved for both low rank coals. Due to higher gasification reactivity, the synthesis gas quality, in view of the total percentage of  $H_2$  and CO, was somehow improved. For example, the total percentage of  $H_2$  and CO was about 55 % under the air-blown mode and 75 % under the oxygen-blown mode for Lignite. The cold gas efficiency was even higher at about 60 % under the air-blown mode and at 85 % under oxygen-blown mode for PRB coal. However, the lower synthesis gas yield was found for Texas Lignite due to low quality (lower carbon content) in these two low rank coal. Higher ash and moisture contents in Texas Lignite will be a big issue for its application in coal gasification processes due to the energy penalty for coal drying and heat loss carried by hot ash discharge. Ash slagging is another problem for Texas lignite with higher ash content. PRB coal may have the same problem due to the energy penalty of the higher moisture content. Kentucky coal should be a better candidate if we could improve its gasification reactivity.



Table 3-1. Theoretical operational parameters and compositions and yields of synthesis gas in the coal gasification process based on heat and mass balance

Coal Gasification (Theoretical calculation)									
Coal	Lignite			PRB			Kentucky Bitu		
Operation parameters									
Operation Mode	Air-blown	Air-blown	Oxygen-blown	Air-blown	Air-blown	Oxygen-blown	Air-blown	Air-blown	Oxygen-blown
Air(or O <sub>2</sub> )/coal ratio, NM <sup>3</sup> /kg	0.68	0.61	0.143	1.38	1.31	0.29	1.57	0.78	0.33
Steam/coal ratio, kg/kg	0.41	0.37	0.4	0.698	0.663	0.698	0.797	0.399	0.797
Carbon conversion efficiency, %	100	90	100	100	95	100	100	90	100
Syngas compositions									
Gas compositions, %									
H <sub>2</sub>	44.7	45.7	61.3	38.3	34.2	52.9	36.4	36.7	53.2
CO	21.6	21.4	29	23.3	26.2	35.9	24	24.8	35.1
CH <sub>4</sub>	0	0	0	0	0	0	0	0	0
CO <sub>2</sub>	7.1	6.9	9.7	7.8	7.3	11.2	8	7.8	11.7
N <sub>2</sub>	26.6	26	0	30.6	32.3	0	31.6	30.7	0
O <sub>2</sub>	0	0	0	0	0	0	0	0	0
Syngas Index									
Dry synthesis gas yield, NM <sup>3</sup> /kgcoal	2.37	2.19	1.74	3.73	3.11	2.59	4.08	3.78	2.79
CO+H <sub>2</sub> , %	66.3	67.1	90.3	61.6	60.4	88.8	60.4	61.5	88.4
H <sub>2</sub> /CO	2.07	2.14	2.11	1.64	1.31	1.47	1.52	1.48	1.52
Calculation presumption:									
Calculation is based on dry syngas basis using coal data in dry basis									
All hydrogen element (H) in coal is converted into hydrogen gas (H <sub>2</sub> )									
Two operation modes included: air-blown and oxygen-blown									

Table 3-2. Theoretical operational parameters and compositions and yields of synthesis gas in the coal gasification process based on heat and mass balance with consideration of heat loss

Coal Gasification (Theoretical calculation with consideration of heat loss)						
Coal	Lignite		PRB		Kentucky Bitu	
Operation parameters						
Operation Mode	Air-blown	Oxygen-blown	Air-blown	Oxygen-blown	Air-blown	Oxygen-blown
Air(or O <sub>2</sub> )/coal ratio, NM <sup>3</sup> /kg	1.1	0.23	2.2	0.46	2.5	0.53
Steam/coal ratio, kg/kg	0.2	0.4	0.56	0.698	0.64	0.64
Carbon conversion efficiency, %	90	90	90	90	90	90
Syngas compositions						
Gas compositions, %						
H <sub>2</sub>	35.6	58.7	27	52	28.5	50.7
CO	14.7	24.9	15.1	28.8	16.6	29.6
CH <sub>4</sub>	0	0	0	0	0	0
CO <sub>2</sub>	10	16.4	10.1	19.2	11.1	19.7
N <sub>2</sub>	39.7	0	47.8	0	43.8	0
O <sub>2</sub>	0	0	0	0	0	0
Syngas Index						
Dry synthesis gas yield, NM <sup>3</sup> /kgcoal	2.7	1.64	4.61	2.41	4.71	2.65
(CO+H <sub>2</sub> ), %	50.3	83.6	42.1	80.8	45.1	88.4
H <sub>2</sub> /CO	2.42	2.36	1.79	1.81	1.72	1.71
Calculation presumption:						
Calculation is based on dry syngas basis using coal data in dry basis						
All hydrogen element (H) in coal is converted into hydrogen gas (H <sub>2</sub> )						
Two operation modes included: air-blown and oxygen-blown						

Table 4-1. Operation parameters and test results of syngas compositions in the coal gasification process (KY bit-1)

Coal Pyrolysis & Partial Gasification (KY bit-1)								
Test NO	1	2	3	5	6	7	8	9
Operation Mode	Air-blown						Oxygen-blown	
Coal	KY bit-1							
Operation Parameters								
	1.27	1.63	1.65	1.31	1.45	1.57	O <sub>2</sub> : 0.305 (O <sub>2</sub> +N <sub>2</sub> : 0.355)	O <sub>2</sub> : 0.315 (O <sub>2</sub> +N <sub>2</sub> : 0.367)
Air or Oxygen/coal ratio, NM <sup>3</sup> /kg								
Steam/coal ratio, kg/kg	0.85	0.85	0.85	0.8	0.8	0.8	0.8	0.8
Particle Size, mm	0.5-0.8	0.5-0.8	0.5-0.8	0.5-0.85	0.5-0.85	0.5-0.85	0.5-0.85	0.5-0.85
Bed Temp, °C	943	935	955	985	989	980	1035	1043
Pressure, bar	1	1	1	1	1	1	1	1
Syngas Compositions								
Gas compositions, %								
H <sub>2</sub>	16.71	33.04	20.5	23.83	20.77	26.03	38.16	35.48
CO	10.62	13.04	9.22	20.94	21.52	18.05	37.03	37.81
CH <sub>4</sub>	4.73	6.6	3.96	2.87	1.98	1.68	1.32	1.11
CO <sub>2</sub>	12.57	7.73	10.66	12.46	12.75	13.6	20.42	22.86
N <sub>2</sub>	55.37	39.59	55.66	39.9	42.98	40.64	3.07	2.74
O <sub>2</sub>	0	0	0	0	0	0	0	0
Syngas Index								
Dry synthesis gas production, NM <sup>3</sup> /kgcoal				2.85	2.88	3.31	1.865	1.903
Carbon conversion efficiency, %	38	34.5	41.2	68.3	71.3	73.9	78.2	80.4
(CO+H <sub>2</sub> ), %	27.33	46.08	29.72	44.77	42.29	44.08	75.19	73.29
H <sub>2</sub> /CO	1.57	2.53	2.22	1.14	0.97	1.44	1.03	0.94

Table 4-2. Operation parameters and test results of syngas compositions in the coal gasification process (KY bit-2)

Coal Pyrolysis & Partial Gasification (KY bit-2)							
Test NO	1	2	3	4	5	6	7
Operation Mode	Air-blown				Oxygen-blown		
Coal	KY bit-2						
	Operation Parameters						
	1.76	1.35	1.45	1.45	1.5	O <sub>2</sub> : 0.312 (O <sub>2</sub> +N <sub>2</sub> : 0.362)	O <sub>2</sub> : 0.315 (O <sub>2</sub> +N <sub>2</sub> : 0.367)
Air or Oxygen/coal ratio, NM³/kg							
Steam/coal ratio, kg/kg	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Particle Size, mm	0.5-0.85	0.5-0.85	0.5-0.85	0.5-0.85	0.5-0.85	0.5-0.85	0.5-0.85
Bed Temp, °C	935	955	970	990	980	1035	1035
Pressure, bar	1	1	1	1	1	1	1
	Syngas Compositions						
Gas compositions, %							
H <sub>2</sub>	14.33	20.97	25.41	25.23	26.23	42.36	43.12
CO	5.66	9.1	23.39	22.68	23.11	39.3	40.83
CH <sub>4</sub>	3.56	4.16	1.37	1.01	1.3	1.07	0.87
CO <sub>2</sub>	3.48	10.11	10.63	10.9	11.21	14.16	12.64
N <sub>2</sub>	72.97	55.66	39.2	40.18	38.15	3.11	3.11
O <sub>2</sub>	0	0	0	0	0	0	0
	Syngas Index						
Dry synthesis gas production, NM³/kgcoal			3.15	3.04	3.25	2.012	2.178
Carbon conversion efficiency, %	34.5	41.2	82.3	81.7	83.9	87.3	85.6
(CO+H <sub>2</sub> ), %	19.99	30.07	48.80	47.91	49.34	81.66	83.95
H <sub>2</sub> /CO	2.53	2.30	1.09	1.11	1.14	1.08	1.06

Table 4-3. Operation parameters and test results of syngas compositions in the coal gasification process (Lignite and PRB)

Coal Pyrolysis & Partial Gasification												
Test NO	1	2	3	4	5	6	7	1	2	3	4	5
Operation Mode	Air-blown				Oxygen-blown			Air-blown			Oxygen-blown	
Coal	Lignite							PRB				
	Operation Parameters							Operation parameters				
Air (oxygen)/coal ratio, NM³/kg	0.905	0.797	0.796	1.1	O <sub>2</sub> : 0.28 (O <sub>2</sub> +N <sub>2</sub> : 0.33)	O <sub>2</sub> :0.35 (O <sub>2</sub> +N <sub>2</sub> : 0.396)	O <sub>2</sub> :0.29 (O <sub>2</sub> +N <sub>2</sub> : 0.341)	0.93	0.93	0.93	O <sub>2</sub> : 0.229 (O <sub>2</sub> +N <sub>2</sub> : 0.33)	O <sub>2</sub> : 0.232 (O <sub>2</sub> +N <sub>2</sub> : 0.269)
Steam/coal ratio, kg/kg	0.45	0.418	0.421	0.466	0.412	0.519	0.483	0.5	0.5	0.5	0.58	0.5
Particle Size, mm	0.1-0.5	0.1-0.5	0.1-0.5	0.1-0.5	0.1-0.5	0.1-0.5	0.1-0.5	0.5-0.8	0.5-0.8	0.5-0.8	0.8-1.2	0.5-0.8
Bed Temp, °C	910	900	900	950	900	950	950	940	928	959	950	940
Pressure, bar	1	1	1	1	1	1	1	1	1	1	1	1
	Syngas Compositions							Syngas Compositions				
Gas compositions, %												
H <sub>2</sub>	32.18	33.25	32.52	27.19	45.6	42.54	40.89	32.88	29.26	31.8	45	46.74
CO	21.56	24.7	23.06	19.71	31.12	32.82	34.27	27.75	30.74	31.17	37.72	40.21
CH <sub>4</sub>	2.67	2.72	2.8	1.41	2.2	1.78	2.36	2.89	1.9	1.99	2.14	1.79
CO <sub>2</sub>	9.04	8.05	8.73	10.53	17.29	18.76	19.58	5.72	3.5	4.46	12.7	9.08
N <sub>2</sub>	34.55	31.28	32.89	41.16	3.79	4.1	2.9	30.76	34.6	30.58	2.45	2.17
O <sub>2</sub>	0	0	0	0	0	0	0	0	0	0	0	0
	Syngas Index							Syngas Index				
Dry synthesis gas production, NM³/kgcoal	2.23	2.208	2.204	2.28	1.379	1.618	1.863	2.39	2.13	2.41	1.852	1.792
Carbon conversion efficiency, %	92.3	91.7	92.6	90.5	95.1	98.6	98.2	91.2	85.7	92.7	95.2	94.5
(CO+H <sub>2</sub> ), %	53.74	57.95	55.58	46.90	76.72	75.36	75.16	60.63	60.00	62.97	82.72	86.95
H <sub>2</sub> /CO	1.49	1.35	1.41	1.38	1.47	1.30	1.19	1.18	0.95	1.02	1.19	1.16

#### 4.5 Co-gasification of Coal and CBM in 2.5" gasifier

Tests under normal gasification conditions for all U.S. coals indicated the ratio of  $H_2$  and CO remains around 1 if we heat losses could be ignored, which was confirmed by the theoretical calculation. Sometimes this ratio was even lower than 1 because of involvement of char gasification by  $CO_2$ , which is generated in the coal combustion processes for autothermic purposes. Co-gasification of coal and methane might be a good option to improve the ratio of  $H_2$  and CO, but must deal with  $CH_4$  conversion efficiency during the co-gasification process and other side reactions such as the reaction between  $CH_4$  and  $CO_2$  and  $O_2$ , which resulted in the unexpected ratio of  $H_2$  and CO in the synthesis produced in the co-gasification process. Moreover, coal char did have a catalytic effect on  $CH_4$  reforming, but not in an efficient way. In the followed-up co-gasification tests, we greatly increased the height of coal char bed in order to increase the residence time of  $CH_4$  with contacting coal char. Test results of co-gasification by combining coal and 100 pure cylinder  $CH_4$  gas in this study, were shown in Table 5. For two Kentucky Bituminous coals, the expected ratio of  $H_2$  and CO at about 2 could be achieved in the 2.5" co-gasification demonstration unit. It was even a little higher than expected due to the ratio of the  $CH_4$  addition. The ratio of the  $CH_4$  addition to air was around 20 % under the air-blown mode and about 100% to the oxygen supply under oxygen-blown mode. In general, higher  $CH_4$  conversion efficiency could be achieved under the oxygen-blown mode than that achieved under the air-blown mode. Under the same operation conditions, higher  $CH_4$  conversion efficiency could be achieved for KY bit-2 than that for KY bit-1 due to higher reactivity of the KY bit-2. Its high reactivity co-gasification process results in larger specific surface areas of coal char in the co-gasifier so that its catalytic effect on  $CH_4$  is improved. The correlation of  $CH_4$  conversion efficiency with the specific surface area of char could be found in a previous chapter. The higher  $CH_4$  conversion efficiency, which was achieved in the 2.5" co-gasifier, is attributed to the longer residence time of  $CH_4$  in the co-gasifier; and the intensive mixture of  $CH_4$  with the coal char by turbulence in the fluidization operation mode in both dense and dilute phases.

Table 5. Operation parameters and test results of syngas compositions in the co-coal gasification process (Kentucky coals)

Co-gasification by Coal & Coal-bed Methane							
Test NO	1	2	3	4	5	6	7
Operatio Mode	Air-blown			oxygen-blown		Air-blown	
Coal	KY bit-2					KY bit-1	
Operation Parameters							
Air or Oxygen/coal ratio, NM³/kg	1.55	1.55	1.55	O₂: 0.326 (O₂+N₂: 0.39)	O₂: 0.326 (O₂+N₂: 0.39)	1.55	1.55
Steam/coal ratio, kg/kg	1.05	1.05	1.05	1.05	1.05	1.05	1.05
CH₄/coal ratio, NM³/kg	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Particle Size, mm	0.5-0.85	0.5-0.85	0.5-0.85	0.5-0.85	0.5-0.85	0.5-0.85	0.5-0.85
Bed Temp, °C	983	995	974	1045	1040	993	998
Pressure, bar	1	1	1	1	1	1	1
Syngas Compositions							
Gas compositions, %							
H₂	23.72	26.88	21.27	49.67	48.85	21.22	25.97
CO	10.71	12.76	9.54	23.22	21.82	9.93	12.1
CH₄	5.33	5.71	3.27	5.36	5.96	4.52	4.16
CO₂	10.1	8.5	9.66	17.87	18.91	6.5	5.37
N₂	50.14	46.14	56.26	3.88	4.46	57.83	52.4
O₂	0	0	0	0	0	0	0
Syngas Index							
Dry synthesis gas production, NM³/kgcoal	3.04	2.85	3.18	2.08	2.04	2.25	2.19
Carbon conversion efficiency, %	68.7	65.2	61.1	69.2	68.5	83.2	82.9
CH₄ conversion efficiency, %	72.3	70.3	81.3	88.1	86.9	83.7	86.2
(CO+H₂), %	34.43	39.64	30.81	72.89	70.67	31.15	38.07
H₂/CO	2.21	2.11	2.23	2.14	2.24	2.14	2.15



#### 4.6 Mercury Capture by Activated Char from Gasification Char Residue

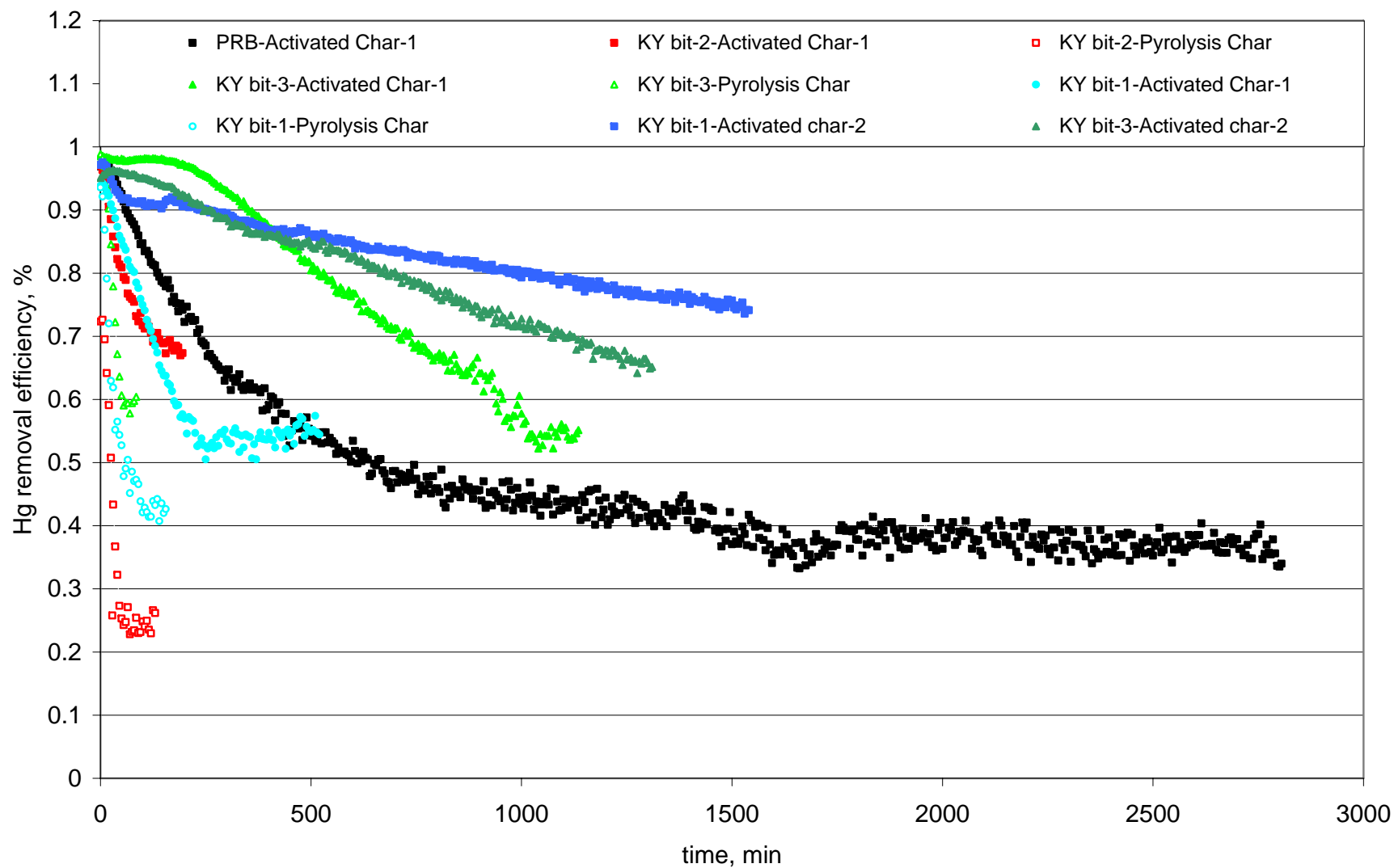
New federal regulations are going to be enacted for trace metal emissions, notably mercury. Depending on the details, such regulations may become an obstacle to using gasification-based technologies since more elemental mercury, which is not easily controlled, is supposed to be higher under the reducing atmosphere in gasification process. The development of carbon-based adsorbents for Hg and other trace metals, which are produced during coal or co-gasification processes seems imperative and promising. This capture technology is likely operated between 150 °C and 300 °C in order to improve or maintain the IGCC efficiency. On the other hand, another source of regulatory uncertainty is the EPA's proposed rule on whether to classify gasification or co-gasification by-products (residues of gasification slag or gasification char) as hazardous waste. Thus, mercury emission control and the economic utilization of potential hazardous gasification residue are imperative for gasification technology and thus preferable in the marketplace. A concept was developed in this study to utilize or recover char residues from the co-gasification process to be Hg adsorbent, which could be used to capture Hg in the synthesis gas stream under desired operational conditions.

Based on the suggested concept, mercury capture by coal char residues was evaluated in this study. Coal char might directly from the coal pyrolysis process, or the followed-up co-gasification process, or those char residues after activation treatment by H<sub>2</sub>O. We also develop some novel Hg adsorbents using activated char as substrate with specific surface area, on which some active additives were doped to enhance their Hg capture capability. PRB chars had very large specific surface area at about 650 NM<sup>2</sup>/kg. All Pyrolysis chars had very low specific surface areas at about 5 NM<sup>2</sup>/kg. Chars from all Kentucky coals had specific surface areas at around 100 NM<sup>2</sup>/kg and 200 NM<sup>2</sup>/kg, which is pretty lower than that of PRB char. Test results were shown in Figure 17, by which the variation of Hg capture efficiency of prepared Hg adsorbents versus time was presented. Generally speaking, Pyrolysis chars had less Hg capture capability than gasification chars and activated char residues because of very low specific surface areas of pyrolysis chars. Activation under H<sub>2</sub>O atmosphere seems to be effective in the increase of specific surface areas of coal char or char residue, which resulted in the improved Hg capture capability over their parent pyrolysis chars or gasification chars. This was also the reason why PRB char has larger Hg capture capability than those of chars derived from Kentucky coals. However, some of activated chars from Kentucky coals with improved specific surface area but still lower than PRB char, those with labels of Activated char-2, presented the better Hg capture capability than that of PRB char. It seems that the

originality of char samples seems to impact their Hg capture capability, such as sulfur content in the original coal. Sulfur was believed to be an active element to promote the Hg capture. It was likely the retained and enriched sulfur species on the surface of Kentucky coal chars enhance their Hg capture capability, even though their specific surface areas was lower than PRB chars. It is likely that the sulfur species, on the surface of generated gasification char, enhanced Hg capture by setting up strong bonding between sulfur and Hg. PRB chars had lower sulfur content because of lower sulfur content in its parent coals. Low rank coal is generally used to prepare good adsorbents because of its activation reactivity resulting in the larger specific surface area with less production cost. From this study, gasification char residues, especially originated from Kentucky coal, could be good candidates for preparation of Hg adsorbents.

By understandings of importance of surface active sites on the Hg capture by char residues, additional tests have been conducted to explore potential chemicals which could enhance surface more active or affinity to Hg. Preliminary tests help us to locate some of active chemicals and enhanced Hg capture performance was achieved. Continuous tests will be pursued recently.

Figure 17. Hg capture performance by coal char residues form gasification and co-gasification process



## 5. CONCLUSION

At the completion of this project, the following conclusions can be drawn on several issues regarding the co-gasification of coal and coal-bed methane:

► For all test coals, co-gasification of coal and simulated methane could generate synthesis gas with the  $H_2/CO$  ratio at nearly 2.0, by which chemicals production through Fischer-Tropsch synthesis could be achieved. Carbon Conversion efficiency of Kentucky coals (KY bit-2) and methane conversion efficiency could be achieved at above 80%, especially in the oxygen-blown mode. Another Kentucky coal (KY bit-1) shows lower carbon conversion efficiency due to its lower gasification reactivity. It could be improved by extending its residence time at the elevated temperature in the gasifier, such as the high temperature Circulating Fluidized Bed Gasifier (CFBG). The gasification selectivity of coal and methane conversion (the cold gas efficiency in the sum of  $H_2$  and CO) could be achieved at above 80% in the oxygen-blown mode. Two low-rank U.S. coals show better reactivity than Kentucky coals, but have a lower gas yield and gas quality because of higher moisture and/or ash content in low-rank coals. The development of high temp (less than ash melting point) CFBG seems imperative for all Kentucky coals in near future.

► Thermodynamics calculation predicts that the methane conversion could be achieved by almost 100% and selectivity (the sum of  $H_2$  and CO) by almost 100% at a temperature range of 900-1050 °C. However, the  $H_2/CO$  ratio is below 1.5 if all possible reactions on  $CH_4$  reforming and partial oxidation occur. The follow-up kinetics study in a 1" testing rig presents the possibility of  $CH_4$  reforming and partial oxidation with a favorable  $H_2/CO$  ratio, which is greater than 5. The higher  $H_2/CO$  in  $CH_4$  reforming and partial oxidation process means less  $CH_4$  in mass is needed to adjust the  $H_2/CO$  ratio in the co-gasification process of coal and coal-bed methane, which is efficient. Ash failed to be a good candidate as a catalyst on  $CH_4$  reforming and partial oxidation due to its low specific surface area available for catalyst reactions. However, coal chars present very promising catalytic performance on  $CH_4$  reforming and partial oxidation because of their larger specific surface area. In this study, no constituents? in fly ashes of coals or special surface properties of coal chars are correlated with the enhanced  $CH_4$  conversion efficiency. It seems that the specific surface area is the only variable for controlling  $CH_4$  conversion efficiency. In the follow-up tests in the 2.5" gasification demonstration unit, addition of methane was below in the dense phase but above the area where the oxygen concentration was enriched to prevent it to burnout.

► Mercury and potentially solid residues, which are both generated in the gasification

process could be enacted by EPA rules because they are dangerous to our environment. In this study, a conceptive development of Hg capture by char residues from gasification process was pursued. Tests indicated that gasification char residue could be re-activated by steam to generate effective Hg adsorbent with its developed pore structure. Most promisingly, all activated char residues, which were derived from Kentucky coals, generally showed enhanced Hg capture capability and even better than char residues from low rank coal. It was likely that the sulfur species on the surface of activated char residue enhanced Hg capture by strong bonding between sulfur and Hg. Low rank coal is generally used to prepare good adsorbent because of its activation reactivity resulting in the larger specific surface area with less production cost. Char residues, which were derived from Kentucky coals, could be good candidates for preparation of Hg adsorbents.

## 6. SUGGESTION

Gasification technology supports national energy security goals by producing ultra-clean power, clean liquid fuels, and chemicals from our nation's most abundant energy resource, coal, as well as from readily available wastes and bio-resources. While regulations on the greenhouse gas (GHG) carbon dioxide (CO<sub>2</sub>) would be an immediate hurdle to deployment of coal plants, gasification plants are in the best position compared to other coal-based alternatives to capture CO<sub>2</sub>. Given the uncertainty of CO<sub>2</sub> regulation, there is industry reluctance to make large investments in projects with high CO<sub>2</sub> emissions, since a cost-effective solution for reducing such emissions is not yet available. Nevertheless, the GHG issue can be an enhancing factor for gasification in the long run because the CO<sub>2</sub> occurs in a concentrated form, making it more amenable to capture<sup>17</sup>. Recent government initiatives regarding gasification technologies may be found in the President's plan on *Hydrogen Production and CO<sub>2</sub> Sequestration*, and the U.S. Department of Energy (DOE)'s plan entitled *Vision 21 and FutureGen*, as well as from our state in Kentucky Governor Ernie Fletcher's 2005 *Comprehensive Energy Strategy*<sup>6</sup> and Kentucky's *Initiative of the American Energy Security Study*<sup>18</sup>.

Refinery applications offer economic advantages that make gasification competitive even at today's natural gas prices. IGCC is by far the cleanest coal-based power system available today. Coal gasification is projected to become the dominant application in the power generation market during the next 12–15 years in the United States and in overseas markets. Gasification technologies also provide opportunities for enhancement and re-powering of existing power plants and the enhancement of power generation at existing sites. Synthesis gas derived from

gasification represents a fuel for fuel cells and a basis for producing clean fuels, with the clean fuels option believed to be the primary option through 2015. A near-term opportunity for gasification technologies is provided by the push for ultra-clean transportation fuels. The combination of gasification with Fischer-Tropsch (F-T) processes has potential in the U.S. liquid fuels market to meet a need for low-sulfur, high-quality diesel fuels. Future regulations are likely to put a high premium on F-T products for use as blending stock<sup>19</sup>.

The relatively low, stable cost of coal and its abundance domestically make coal gasification the ultimate dominant market for gasification technology. Kentucky has been one of the top three coal producers in the United States for the last 50 years. Kentucky coal has low ash content and high BTU heating value, which is superior to two other kinds of coal in the U.S. with leading production (i.e., PRB and Lignite) because their high ash content and low BTU heating value can be a problem in gasification plants. Gasification is environmentally superior to incineration for disposal of municipal and industrial wastes, and with some development can emerge an economic “winner.” Gasification offers an effective means to convert highly toxic substances, like polychlorinated biphenyls (PCB), into salable by-products. With improvements in capital costs, gasification will have significant market potential.

The Institute for Combustion Science and Environmental Technology at Western Kentucky University is beginning to build an advanced research and demonstration platform for energy utilization of biomass, coal and solid wastes by gasification technologies. The available facilities at the ICSET include the Advanced Circulating Fluidized Bed Demonstration Facility (CFBDF) funded by the U.S. Department of Energy (DOE); the Co-utilization Facility of Coal and Coal-bed Methane (CFCCM) funded by the Kentucky Office Energy Policy (KOEP); and the Advanced Coal Gasification Project (ACGP) funded by East Kentucky Power Cooperative (EKPC) and Warren Rural Electric Cooperative. Among them, the CFBDF can be used to demonstrate the scale-up of the proposed technology on a pilot-scale. The goals in this suggestion are to develop a new gasification concept with feedstock-flexibility and higher carbon conversion efficiency for applications that use feedstock with low energy density (biomass and solid waste) and lower gasification reactivity (Kentucky coals). Co-gasification, which has been explored in the present study, will be the main operation mode in this new gasification concept. The new concept is also to develop low-temperature, non-slugging gasifiers to reduce plant capital and operating costs, to solve slugging problem and to maintain heat loss from discharge char or ash, yet still maintain higher carbon conversion efficiency. The viable means to achieve this goal will be the modification of an available 2.5” gasification unit into the 2.5” Circulating Fluidized Bed Gasification unit.

This will be accomplished with the recirculation of gasification char residues back to the gasifier through cyclones and a stand leg. An L-valve (a kind of two-phase flow control valve) will be used to control the re-circulating rate of char. It performs like a circulating fluidized bed gasifier, but at a recirculation rate much higher than that of a general circulating fluidized bed gasifier. The purpose of char or ash recirculation is to extend residence time of char residues inside the gasifier to fulfill its total carbon conversion efficiency. Recirculation is a also key step in co-gasification process due to our belief that coal char can act as a catalyst to improve reforming of methane or biomass gasification and thus improve quality of synthesis gas. The previous DOE funded CFBDF will be used to demonstrate the scale-up of the proposed technology in the pilot-scale demonstration. The other considerations during modification are: 1) investigation of the co-feed system which have the flexibility to feed different solid feedstocks separately and together; 2) development of slurry type of co-feeder; 3) development of new and/or improved approaches for dewatering and increasing the density of low-BTU alternative feedstock (biomass); 4) development of low-cost briquetting techniques;

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